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HAYASHIDA KAZUYOSHI**(54) SUBSTRATE CLEANING AGENT****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a metal corrosion inhibitor, which is added to a cleaning agent particularly for the substrate surface having a copper electric wiring thereon, and can effectively remove metal impurities (copper oxide) on the surface, without causing corrosion and oxidation of the copper electric wiring.

**SOLUTION:** The metal corrosion inhibitor includes amino acid having a thiol group in a molecular, like cysteine; or amino acid derivatives which include an N-acyl compound of amino acid like N-acetylcysteine, and a carboxylic acid ester of amino acid like a cysteine methyl ester. The substrate cleaning agent includes the above metal corrosion inhibitor.

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**[JP,2003-013266,A]**

**CLAIMS**

[Claim(s)]

[Claim 1] Metal corrosion inhibitor which comes to contain in intramolecular the amino acid which has a thiol group, or its derivative.

[Claim 2] Metal corrosion inhibitor according to claim 1 which is an aqueous solution.

[Claim 3] Metal corrosion inhibitor according to claim 1 or 2 whose amino acid which has a thiol group in intramolecular is a cysteine or a homocysteine.

[Claim 4] Metal corrosion inhibitor given in any of claims 1-3 whose amino acid derivatives are N-acyl object of amino acid, or a carboxylate object of amino acid they are.

[Claim 5] The metallic corrosion inhibitor according to claim 4 into which the acyl group of the carboxylic-acid origin of N-acyl object is introduced.

[Claim 6] Metal corrosion inhibitor according to claim 4 whose N-acyl object is N-alkanoyl object or N-ARARUKA noil object.

[Claim 7] Metal corrosion inhibitor according to claim 4 whose N-acyl object is N-acetyl object.

[Claim 8] Metal corrosion inhibitor according to claim 4 whose ester object is an alkyl ester object or an aralkyl ester object.

[Claim 9] Metal corrosion inhibitor according to claim 4 whose ester object is a low-grade alkyl ester object or a benzyl ester object.

[Claim 10] Furthermore, metal corrosion inhibitor given in any of claims 1-9 which come to contain at least one of an organic acid, an amine, an inorganic alkali compound, a chelating agent, and surfactants they are.

[Claim 11] Metal corrosion inhibitor according to claim 10 whose organic acids are JI thru/or tricarboxylic acid.

[Claim 12] Metal corrosion inhibitor according to claim 10 whose organic acids are monochrome dihydroKISHIJI thru/or tricarboxylic acid.

[Claim 13] Metal corrosion inhibitor according to claim 10 an amine is [ corrosion inhibitor ] in any of alkylamine, dialkyl amine, hydroxy alkylamine, alkylene diamine, dialkylenetriamine, a thoria RUKIREN tetramine, an alkylamine-alkylene oxide addition product, and tetra-alkylammonium hydroxide.

[Claim 14] Metal corrosion inhibitor according to claim 10 whose inorganic alkali compound is a nitrogen content inorganic alkali compound.

[Claim 15] Metal corrosion inhibitor according to claim 14 it is [ corrosion inhibitor ] that as which a nitrogen content inorganic alkali compound is chosen from the group which it becomes from a hydroxylamine, a hydrazine, ammonia, and these salts.

[Claim 16] Metal corrosion inhibitor according to claim 10 whose chelating agents are amino polycarboxylic acid or/and phosphonic acid.

[Claim 17] Metal corrosion inhibitor according to claim 16 whose amino polycarboxylic acid is straight chain mold amino polycarboxylic acid or/and annular amino polycarboxylic acid.

[Claim 18] Metal corrosion inhibitor according to claim 17 whose straight chain mold amino polycarboxylic acid is EDTA (ethylenediaminetetraacetic acid), EDDA (ethylenediamine 2 acetic acid), EDTA-OH (hydroxy ethylenediamine triacetic acid), GEDTA (glycol ether diamine tetraacetic acid), DTPA (diethylenetriamine pentaacetic acid), IDA (iminodiacetate), methyl-EDTA (diaminopropane tetraacetic acid), NTA (nitrilotriacetic acid), TTHA (triethylenetetramine 6 acetic acid), its ammonium salt, or complex salt with an amine.

[Claim 19] Metal corrosion inhibitor according to claim 17 whose annular amino polycarboxylic acid is CyDTA (trans-cyclohexyl diamino tetraacetic acid), its ammonium salt, or complex salt with an amine.

[Claim 20] Metal corrosion inhibitor according to claim 16 whose phosphonic acid is Pori phosphonic acid or/and amino poly phosphonic acid.

[Claim 21] Metal corrosion inhibitor according to claim 20 whose Pori phosphonic acid is NTPO (nitrilotrismethylene phosphonic acid), HEDPO (hydroxy ECHIRIDENJI (methylene phosphonic acid)), its ammonium salt, or complex salt with an amine.

[Claim 22] Metal corrosion inhibitor according to claim 20 whose amino poly phosphonic acid is EDDPO (ethylene JIAMINJI (methylene phosphonic acid)), EDTPO (ethylenediamine tetrapod (methylene phosphonic acid)), PDTPO (diaminopropane tetrapod (methylene phosphonic acid)), DETPPO (diethylenetriamine PENTA (methylene phosphonic acid)), TTHPO (triethylenetetramine hexa (methylene phosphonic acid)), its ammonium salt, or complex salt with an amine.

[Claim 23] Metal corrosion inhibitor according to claim 10 whose surfactant is the



Nonion system surfactant or an anion system surfactant.

[Claim 24] the Nonion system surfactant has a polyoxyalkylene group in a molecule — coming out — a certain metal corrosion inhibitor according to claim 23.

[Claim 25] Metal corrosion inhibitor according to claim 23 whose Nonion system surfactants are polyoxyalkylene alkyl ether or polyoxyalkylene poly alkyl aryl ether.

[Claim 26] Metal corrosion inhibitor according to claim 23 which is what has the radical chosen from the group which an anion system surface active agent becomes from a sulfonic group, a carboxyl group, a phosphonic acid radical, and a sulfo KISHIRU radical.

[Claim 27] Metal corrosion inhibitor according to claim 26 whose anion system surfactants are an alkyl sulfonic acid, alkylarylsulfonic acid, alkyl-sulfuric-acid ester, an alkyl aryl sulfate, polyoxyalkylene alkyl-sulfuric-acid ester, a polyoxyalkylene alkyl aryl sulfate, an alkyl carboxylic acid, alkyl aryl carboxylic acids, or these salts.

[Claim 28] The processing agent which comes to contain metal corrosion inhibitor given in any of claims 1-27 they are.

[Claim 29] The processing agent according to claim 28 which is the object for substrates to which a processing agent has the copper covering section on a front face.

[Claim 30] The processing agent according to claim 29 whose substrate is a semi-conductor substrate.

[Claim 31] The art of this substrate characterized by processing a substrate by the processing agent according to claim 28.

[Claim 32] The art according to claim 31 whose substrate is what has the copper covering section on a front face.

[Claim 33] The art according to claim 32 whose substrate is a semi-conductor substrate.

[Claim 34] The cleaning agent which comes to contain metal corrosion inhibitor given in any of claims 1-27 they are.

[Claim 35] The cleaning agent according to claim 34 whose cleaning agent is the object for substrates which has the copper covering section on a front face.

[Claim 36] The cleaning agent according to claim 34 whose substrate is a semi-conductor substrate.

[Claim 37] The washing approach of this substrate characterized by washing a substrate with a cleaning agent according to claim 34.

[Claim 38] The washing approach according to claim 37 that a substrate is a semi-conductor substrate which has the copper covering section on a front face.

[Claim 39] The washing approach according to claim 38 that a substrate is a semi-conductor substrate.

[Claim 40] The art of this substrate characterized by processing the substrate concerned by the processing agent according to claim 28 after giving the semi-conductor substrate which has the copper covering section on a front face to chemical physical polish processing (CMP).

[Claim 41] The art of this substrate characterized by processing the substrate concerned by the processing agent according to claim 28, and subsequently washing the substrate concerned with a semi-conductor substrate cleaning agent after giving the semi-conductor substrate which has the copper covering section on a front face to chemical physical polish processing (CMP).

[Claim 42] The washing approach of this substrate characterized by washing the substrate concerned with a cleaning agent according to claim 34 after giving the semi-conductor substrate which has the copper covering section on a front face to chemical physical polish processing (CMP).

## **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the cleaning agent and the washing approach on metal corrosion inhibitor and the substrate front face which used this, and the front face of a substrate where copper wiring was especially given to the front face.

[0002]

[Description of the Prior Art] In recent years, detailed-ization is progressing with high integration and the structure of LSI is the multilayer structure which metal wiring etc. put on the semi-conductor front face in many steps. Moreover, modification in copper with more low electric resistance (Cu) from the aluminum of the former [ wiring / which is used ] is proposed.

[0003] The so-called chemical physical polish technique (Cu-CMP) which grinds and carries out flattening of the semi-conductor substrate physically is used for the process which manufactures the semi-conductor which has the multilayer structure by which copper wiring was continued and given to the multilayer on the front face, oxidizing Metal Cu.

[0004] On the other hand, the insulator layer (silicon oxide) which isolates Cu wiring and each Cu wiring is in the unreserved condition, and the wafer front face after a Cu-CMP process is polluted with a lot of metal impurities by the semi-conductor front face after a Cu-CMP process. It originates in adsorbing on an insulator layer and Cu shaved off by CMP remaining as a metallic oxide (copper oxide), as for metal impurity

contamination.

[0005] Thus, if a metallic oxide (copper oxide) remains on an insulator layer, a copper element is spread in an insulator layer in heat treatment at a back process, the property of a device deteriorates because insulation falls, and a device will be destroyed in order for isolated wiring to raise connection, i.e., short-circuit, when contamination is remarkable. Therefore, before progressing to degree process, it is necessary to remove a metallic oxide (copper oxide).

[0006] In order to remove the above-mentioned \*\*\*\* metal impurity by the above reason, the washing process after a Cu-CMP process is indispensable.

[0007] On the other hand, the metal copper on the front face of a semi-conductor will have high activity, and by few oxidizing power, it is corroded easily, and wiring resistance will increase or it will cause an open circuit. For this reason, in the washing process after a Cu-CMP process, if the penetrant remover which uses as a principal component inorganic acids used as a penetrant remover for semi-conductors, such as a hydrochloric acid, fluoric acid, etc. with comparatively strong oxidizing power, is used conventionally, since not only copper oxide but the metal copper of wiring which adhered on the insulator layer will be dissolved, use of the acid penetrant remover concerned is not desirable. Moreover, although the cleaning agent of a copper solvent action which uses organic acids with comparatively weak oxidizing power, such as oxalic acid and a citric acid, as a principal component is also weak compared with an inorganic acid, since it had the copper solvent action, the low-concentration organic acid needed to be used as much as possible. For this reason, since the solvent power of a metallic oxide also declined when an organic acid is used by low concentration, the semi-conductor front face needed to be washed [ long duration ].

[0008] In order to cancel such a fault, it is known by adding various metal corrosion inhibitor to a cleaning agent that the corrosion of the metal copper on a semi-conductor front face can be prevented.

[0009] For example, the aromatic series system compound which makes benzotriazols and imidazole derivatives representation is indicated by JP,7-79061,A. However, the copper corrosion prevention effectiveness of these compounds is low, and the prevention effectiveness is accepted only by high concentration. However, the compound concerned had the low solubility to water, and it was difficult to add these compounds by high concentration in the ultrapure water generally used as a diluent in case the cleaning agent for semi-conductors is used. Moreover, in order to have used these compounds by high concentration, alkali solubilizing agents, such as an amine, the organic solvent of an alcoholic system, etc. were needed, but these solubilizing agents

and an organic solvent were difficult to use it in order to have a bad influence on a washing property.

[0010] Moreover, ring compounds, such as mercaptoimidazole and a mercapto thiazole, are indicated by JP,2000-87268,A and JP,2000-282096,A. However, if it combines with the copper on the front face of a semi-conductor, since a copper front face will serve as hydrophobicity and these compounds will prevent the attack of a cleaning agent, it becomes difficult to remove these compounds. Thus, while the organic substance like these compounds had remained on the copper front face, when the semi-conductor received heat treatment in a next process, the time of device actuation, etc., the organic substance concerned carried out combustion, explosion, etc., and there was a problem in the problem that a serious defect will arise, safety [ as opposed to / toxicity is strong and / the body or an environment ], etc.

[0011] Furthermore, the fatty alcohol system compound which the carbon which had the sulfhydryl group in molecules, such as mercaptoethanol and mercapto glycerol, and the sulfhydryl group concerned has combined with JP,2000-273663,A, and the carbon which the hydroxyl group has combined have adjoined and combined is indicated. However, although a possibility of having effect harmful to people's health and ecosystem compared with the conventional thing is made for the purpose of offering little metal corrosion inhibitor from the problem about effect, environmental pollution, etc. in recent years to the body, invention indicated by JP,2000-273663,A A problem is still in safety, and these compounds have an unpleasant smell, even when it is added and used into a water solution, and toxicity is strong and they are not [ vapor pressure is comparatively low and ] practical.

[0012]

[Problem(s) to be Solved by the Invention] This invention is what was made in view of the above-mentioned \*\*\*\*\* situation. Metal corrosion inhibitor with safety high [ having a good metallic corrosion prevention operation ], And the art of the substrate concerned which can prevent the oxidation and corrosion of copper wiring in the substrate front face and the substrate front face on which copper wiring was especially given to the front face using this, The washing approach of a substrate that the corrosion and oxidation of copper wiring on the front face of a substrate concerned can be prevented in a list, and the metal impurity (copper oxide) of the front face concerned can be effectively removed in it is offered.

[0013]

[Means for Solving the Problem] This invention consists of the following configurations.

[0014] (1) Metal corrosion inhibitor which comes to contain in intramolecular the

amino acid which has a thiol group, or its derivative.

[0015] (2) The processing agent which comes to contain the metal corrosion inhibitor of a publication in the above (1).

[0016] (3) The art of this substrate characterized by processing a substrate by the processing agent of a publication to the above (2).

[0017] (4) The cleaning agent which comes to contain the metal corrosion inhibitor of a publication in the above (1).

[0018] (5) The washing approach of this substrate characterized by washing with a cleaning agent given [ a substrate ] in the above (4).

[0019] (6) The art of this substrate characterized by processing the substrate concerned by the processing agent of a publication to the above (2) after giving the semi-conductor substrate which has the copper covering section on a front face to chemical physical polish processing (CMP).

[0020] (7) The art of this substrate characterized by processing the substrate concerned by the processing agent of a publication to the above (2), and subsequently washing the substrate concerned with a semi-conductor substrate cleaning agent after giving the semi-conductor substrate which has the copper covering section on a front face to chemical physical polish processing (CMP).

[0021] (8) The washing approach of this substrate characterized by washing with a cleaning agent given [ the substrate concerned ] in the above (4) after giving the semi-conductor substrate which has the copper covering section on a front face to chemical physical polish processing (CMP).

[0022] Safety is [ whose amino acid which has a thiol group in intramolecular or its derivative has a good metallic corrosion prevention operation as a result of repeating research wholeheartedly that this invention person etc. should attain the above-mentioned purpose ] high, If a substrate is processed using the cleaning agent containing amino acid or its derivative concerned in a list The corrosion or oxidation of copper wiring are not caused for a substrate front face and the substrate front face where copper wiring was especially given to the front face, but it came to complete a header and this invention for the ability of the metal impurity (copper oxide) of the front face concerned to be removed effectively.

[0023] The amino acid (it may be hereafter written as the amino acid concerning this invention) which has a thiol group in the intramolecular concerning this invention has a thiol group, a carboxyl group, and an amino group in intramolecular, and the compound specifically shown by the following general formula [1] is mentioned.

[0024]

[Formula 1]

[0025] (R shows a low-grade alkylene group among a formula.)

[0026] as the low-grade alkylene group shown by R in a general formula [1] — a methylene group, ethylene, a trimethylene radical, a tetramethylen radical, a pentamethylene radical, a hexamethylene radical, a propylene radical, a butylene radical, a methyl methylene group, ethyl ethylene, a methyl ethylene radical, a methyl propylene radical, an ethyl propylene radical, and a pentene radical — it passes and the low-grade alkylene group of the shape of a straight chain, such as a xylene radical the shape of branching, and the annular carbon numbers 1-6 be mentioned to a xylene radical, a cyclo pentene radical, and cyclo. Especially, the alkylene group (a methylene group, ethylene, a trimethylene radical, a tetramethylen radical, a pentamethylene radical, hexamethylene radical) of the shape of a straight chain of carbon numbers 1-6 is desirable, and a methylene group or especially ethylene is desirable.

[0027] the amino acid which has a thiol group in the intramolecular concerning this invention — a commercial item (for example, product made from Wako Pure Chem Industry) — you may use — the very thing — according to a well-known approach, it may prepare suitably and you may use.

[0028] As a compound shown by the above-mentioned general formula [1], a cysteine, a homocysteine, etc. are mentioned and, as for these, even the mixture of D object from which a mixing ratio differs also with D object, L bodies, or DL object, respectively, and L bodies is more specifically usable.

[0029] Although it will not be limited as a derivative of the amino acid which has a thiol group in the intramolecular in above-mentioned \*\*\*\* and above-mentioned this invention especially if it has a metallic corrosion prevention operation, the carboxylate object of the amino acid concerning N-acyl object or this invention of amino acid which relates, for example to this invention etc. is mentioned.

[0030] An acyl group is introduced into the hydrogen atom of the amino group which the amino acid concerning \*\*\*\* this invention described above as N-acyl object of the amino acid concerning this invention has. As shown in the following general formula [2], specifically, an acyl group is introduced into the hydroxyl group of the amino group in the above-mentioned general formula [1].

[0031]

[Formula 2]

[0032] (R1 shows an acyl group among a formula, and R is the same as the above.)

[0033] As an acyl group shown by R1 in the acyl group or general formula [2] introduced into the hydrogen atom of the amino group which the amino acid concerning this invention has The shape of a straight chain, the shape of branching, and annular are sufficient. For example, a formyl group, an acetyl group, A propionyl radical, a butyryl radical, an isobutyryl radical, a valeryl radical, an iso valeryl radical, A pivaloyl radical, a hexa noil radical, a cyclo propionyl carbonyl group, The thing of the saturation aliphatic series monocarboxylic acid origin of the carbon numbers 1-6, such as a cyclopentyl carbonyl group and a cyclohexyl carbonyl group, For example, an acryloyl radical, a PUROPIO roil radical, a methacryloyl radical, a KUROTO noil radical, The thing of the partial saturation aliphatic series monocarboxylic acid origin of the carbon numbers 3-7, such as an iso KUROTO noil radical, For example, benzoyl, a naphthoyl radical, a pen TAREN carbonyl group, an in DEREN carbonyl group, An azulene carbonyl group, a HEPUTAREN carbonyl group, an indacene carbonyl group, An anthracene carbonyl group, a phenanthrene carbonyl group, a triphenylene carbonyl group, A pyrene carbonyl group, a naphthacene carbonyl group, a PIRIREN carbonyl group, the carbon numbers 7-23, such as a pentacene carbonyl group, — desirable — the thing of the aromatic series monocarboxylic acid origin of carbon numbers 7-12 — For example, a phenylmethyl carbonyl group, a phenylethyl carbonyl group, A phenylpropyl carbonyl group, a phenyl isopropyl carbonyl group, A phenyl butyl carbonyl group, a phenyl isobutyl carbonyl group, a phenyl pentyl carbonyl group, A phenyl isopentyl carbonyl group, a phenyl neopentyl carbonyl group, A phenyl hexyl carbonyl group, a phenyl iso hexyl carbonyl group, A phenylethyl pentyl carbonyl group, a phenylmethyl pentyl carbonyl group, A phenyl dimethyl butyl carbonyl group, a phenylethyl butyl carbonyl group, A phenyl heptyl carbonyl group, a phenylmethyl hexyl carbonyl group, A phenyl dimethyl pentyl carbonyl group, a phenyl octyl carbonyl group, A phenyl nonyl carbonyl group, a phenyl DESHIRU carbonyl group, a phenyl undecyl carbonyl group, A phenyl dodecyl carbonyl group, a phenyl tridecyl carbonyl group, A phenyl cyclo propylcarbonyl radical, a phenyl cyclopentyl carbonyl group, A phenyl cyclohexyl carbonyl group, a phenyl cyclohexyl carbonyl group, A phenyl cycloheptyl carbonyl group, a phenyl cyclo octyl carbonyl group, A phenyl cyclo nonyl carbonyl group, a phenyl cyclodecyl carbonyl group, the carbon numbers 7-20, such as a phenyl cyclo

undecyl carbonyl group, a phenyl cyclo dodecyl carbonyl group, and a phenyl cyclo tridecyl carbonyl group, — the thing of the aralkyl monocarboxylic acid origin of carbon numbers 7-13 etc. is mentioned preferably. In addition, in the ring of the above-mentioned acyl group of the \*\*\*\* aromatic series monocarboxylic acid origin, or the acyl group of the aralkyl monocarboxylic acid origin, you may have low-grade alkyl groups, such as a methyl group and an ethyl group, etc. as a substituent. Also in the above-mentioned \*\*\*\* acyl group, the thing of the saturation aliphatic series monocarboxylic acid origin and the thing of the aralkyl monocarboxylic acid origin are desirable, are a thing of the saturation aliphatic series monocarboxylic acid origin more preferably, and are a thing of the straight chain-like saturation aliphatic series monocarboxylic acid origin still more preferably. Also in the acyl group of the straight chain-like saturation aliphatic series monocarboxylic acid origin, especially an acetyl group is desirable.

[0034] moreover, N-acyl object of the amino acid which has a thiol group in the intramolecular concerning this invention — a commercial item (for example, product made from Wako Pure Chem Industry) — you may use — the very thing — according to a well-known approach, it may prepare suitably and you may use.

[0035] As an N-acyl object of the amino acid concerning this invention To the hydrogen atom of the amino group which the amino acid concerning this invention has N-ARARUKA noil object with which the acyl group of N-alkanoyl object (that whose R1 in a general formula [2] is the acyl group of the saturation aliphatic series monocarboxylic acid origin) with which the acyl group of the saturation aliphatic series monocarboxylic acid origin was introduced, and the aralkyl monocarboxylic acid origin was introduced (That whose R1 in a general formula [2] is the acyl group of the aralkyl monocarboxylic acid origin) is desirable, and is N-alkanoyl object more preferably. Still more preferably It is N-straight chain alkanoyl object (that whose R1 in a general formula [2] is the acyl group of the straight chain-like saturation aliphatic series monocarboxylic acid origin) with which the acyl group of the straight chain-like saturation aliphatic series monocarboxylic acid origin was introduced into the hydrogen atom of the amino group which the amino acid concerning this invention has. Especially N-acetyl object (that whose R1 in a general formula [2] is an acetyl group) with which the acetyl group was introduced into the hydrogen atom of the amino group which the amino acid concerning this invention has especially is desirable. As an example of N-acyl object (compound shown by the general formula [2]) of the amino acid concerning this invention For example, N-acetylcysteine, N-butyryl cysteine, N-cyclohexyl carbonyl cysteine, N-PUROPIO roil cysteine, N-KUROTO noil cysteine,



N-benzoyl cysteine, N-naphthoyl cysteine, N-phenylmethyl carbonyl cysteine, N-phenyl butyl carbonyl cysteine, N-phenyl cyclohexyl carbonyl cysteine, N-acetyl homocysteine, N-butyryl homocysteine, N-cyclohexyl carbonyl homocysteine, N-PUROPIO roil homocysteine, N-KUROTO noil homocysteine, N-benzoyl homocysteine, N-naphthoyl homocysteine, N-phenylmethyl carbonyl homocysteine, N-phenyl butyl carbonyl homocysteine, N-phenyl cyclohexyl carbonyl homocysteine, etc. are mentioned, and, as for these, even the mixture of D object from which a mixing ratio differs also with D object, L bodies, or DL object, respectively, and L bodies is usable.

[0036] The carboxyl group which the amino acid concerning \*\*\*\*\* this invention described above as the carboxylate object of the amino acid concerning this invention has is esterified. As shown in the following general formula [2], specifically, an acyl group is introduced into the hydroxyl group of the carboxyl group in the above-mentioned general formula [1].

[0037]

[Formula 3]

[0038] (R2 shows hydrocarbon residue among a formula, and R is the same as the above.)

[0039] In a general formula [3], as hydrocarbon residue shown by R2, as long as it is the radical of monovalence, any of aliphatic series, aromatic series, aroma aliphatic series, or an alicycle group are sufficient, and as aliphatic series in aliphatic series and aroma aliphatic series, it may be [ being saturation ] unsaturated, or the shape of the shape of a straight chain and branching has. As a typical thing of these, the alkyl group of the shape of a straight chain, the shape of branching, annular saturation, or partial saturation, an aryl group, an aralkyl radical, an alkenyl radical, etc. are mentioned, for example. The thing of 1-4 is mentioned more preferably. as an alkyl group — usually — the thing of carbon numbers 1-10 — desirable — the thing of 1-6 — specifically For example, a methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl radical, an iso-pentyl radical, a sec-pentyl radical, a tert-pentyl radical, A neopentyl radical, n-hexyl group, an iso-hexyl group, 3-methyl pentyl radical, 2-methyl pentyl radical, 1, 2-dimethyl butyl, a sec-hexyl group, A tert-hexyl group, n-heptyl radical, an iso-heptyl radical, a sec-heptyl radical, n-octyl radical, an iso-octyl radical, a sec-octyl radical, n-nonyl radical, n-decyl group, a cyclo

propyl group, a cyclopentyl group, a cyclohexyl radical, a cycloheptyl radical, a cyclooctyl radical, a cyclodecyl radical, etc. are mentioned. As an aryl group, the thing of carbon numbers 6-14 is usually mentioned, a phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 2, 3-xylyl group, 2, 4-xylyl group, 2, 5-xylyl group, 2, 6-xylyl group, 3, 5-xylyl group, a naphthyl group, an anthryl radical, etc. specifically mention, and it is \*\*\*\*. as an aralkyl radical — usually — the thing of carbon numbers 7-12 — the thing of 7-10 is mentioned preferably and, specifically, benzyl, a phenethyl radical, a phenylpropyl radical, phenyl butyl, a phenyl hexyl group, a methylbenzyl radical, a methyl phenethyl radical, ethyl benzyl, etc. are mentioned. In addition, in the ring of the above-mentioned \*\*\*\* aryl group or an aralkyl radical, you may have low-grade alkyl groups, such as a methyl group and an ethyl group, a halogen atom, a nitro group, the amino group, etc. as a substituent. As an alkenyl radical, the thing of 2-10 is usually mentioned. Specifically For example, a vinyl group, an allyl group, 1-propenyl radical, an iso-propenyl radical, 3-butenyl group, 2-butenyl group, 1-butenyl group, 1, 3-swine dienyl radical, 4-pentenyl radical, 3-pentenyl radical, 2-pentenyl radical, 1-pentenyl radical, A 1, 3-pentadienyl radical, 2, 4-pentadienyl radical, 1, and 1-dimethyl-2-propenyl radical, A 1-ethyl-2-propenyl radical, 1, and 2-dimethyl-1-propenyl radical, A 1-methyl-1-butenyl group, a 5-hexenyl radical, a 4-hexenyl radical, A 2-hexenyl radical, a 1-hexenyl radical, a 1-methyl-1-hexenyl radical, A 2-methyl-2-hexenyl radical, the 3-methyl 1, 3-hexa dienyl radical, 1-heptanyl radical, 2-octenyl group, 3-NONENIRU radical, 4-decenyl radical, 2-cyclo pentenyl radical, 2, 4-cyclopentadienyl group, 1-cyclohexenyl group, 2-cyclohexenyl group, 3-cyclohexenyl group, 2-cycloheptenyl group, 2-cyclo NONENIRU radical, 3-cyclo decenyl radical, etc. are mentioned. Especially, an alkyl group and an aralkyl radical are desirable, are the low-grade alkyl group and benzyl of carbon numbers 1-6 more preferably, and are a low-grade alkyl group of carbon numbers 1-6 still more preferably.

[0040] the carboxylate object of the amino acid which has a thiol group in the intramolecular concerning this invention — a commercial item (for example, product made from Wako Pure Chem Industry) — you may use — the very thing — according to a well-known approach, it may prepare suitably and you may use.

[0041] As a carboxylate object of the amino acid concerning this invention To the carboxyl group which the amino acid concerning this invention has The aralkyl ester object (that whose R2 in a general formula [3] is an aralkyl radical) with which the alkyl ester object (that whose R2 in a general formula [3] is the alkyl group) and aralkyl radical into which the alkyl group was introduced were introduced is desirable. To the carboxyl group which the amino acid more preferably applied to this invention has It is

the benzyl ester object (that whose R2 in a general formula [3] is benzyl) with which low-grade alkyl ester \*\*\*\* (that whose R2 in a general formula [3] is the low-grade alkyl group of carbon numbers 1-6) and benzyl into which the alkyl group of carbon numbers 1-6 was introduced were introduced. Furthermore, it is a low-grade alkyl ester object preferably. As an example of the carboxylate object (compound shown by the general formula [3]) of the amino acid concerning this invention For example, cysteine methyl ester, cysteine ethyl ester, cysteine isobutyl ester, Cysteine n-hexyl ester, cysteine cyclohexyl ester, Cysteine phenyl ester, cysteine naphthyl ester, cysteine benzyl ester, Cysteine methylbenzyl ester, cysteine vinyl ester, cysteine 3-butenyl ester, Cysteine 3-cyclohexenyl ester, homocysteine methyl ester, Homocysteine ethyl ester, homocysteine isobutyl ester, Homocysteine n-hexyl ester, homocysteine cyclohexyl ester, Homocysteine phenyl ester, homocysteine naphthyl ester, Homocysteine benzyl ester, homocysteine methylbenzyl ester, Homocysteine vinyl ester, homocysteine 3-butenyl ester, homocysteine 3-cyclohexenyl ester, etc. are mentioned, and, as for these, even the mixture of D object from which a mixing ratio differs also with D object, L bodies, or DL object, respectively, and L bodies is usable.

[0042] The amino acid which has a thiol group in the intramolecular concerning above-mentioned \*\*\*\* this invention, or its derivative may be used independently, or two or more sorts, it may combine suitably and it may be used.

[0043] Although the amount of the amino acid which has a thiol group in intramolecular, or its derivative used does not generally have \*\*\*\*\* since it changes with the class of the amino acid which has a thiol group in intramolecular, or its derivative, surface areas of the substrate processed, etc., it is 0.0001 - 10 % of the weight usually 0.0001 - 0.5 % of the weight more preferably 0.0001 to 1% of the weight.

[0044] The metal corrosion inhibitor of this invention comes to contain in the intramolecular concerning above-mentioned \*\*\*\* this invention the amino acid which has a thiol group, or its derivative. Moreover, the metal corrosion inhibitor of this invention is usually in the condition of an aqueous solution, and is prepared by making water carry out the addition dissolution of the amino acid concerning this invention concerned, or its derivative.

[0045] As an approach of dissolving the amino acid concerning this invention, or its derivative in water, the approach of adding the amino acid concerning this invention which dissolved separately, for example into water, or its derivative, the approach of adding the amino acid concerning this invention or its derivative in direct water, and dissolving and stirring, etc. are mentioned.

[0046] Thus, as for the prepared metal corrosion inhibitor of this invention, it is

desirable to perform filtration processing etc. before use. Moreover, although the water used here should just be refined by distillation, ion exchange treatment, etc., the so-called ultrapure water used in this field is more desirable.

[0047] Furthermore, into the metal corrosion inhibitor concerning this invention, the reagents usually used in this field in addition to the amino acid concerning above-mentioned \*\*\*\* this invention or its derivative can be used. As such reagents, they are an organic acid, an amine, an inorganic alkali compound, a chelating agent, a surfactant, etc., for example.

[0048] That what is necessary is just what is usually used in this field as an organic acid used in this invention Although not limited especially, for example Oxalic acid, a malonic acid, a succinic acid, a glutaric acid, An adipic acid, a pimelic acid, a suberic acid, a 2-n-butyl malonic acid, a maleic acid, The dicarboxylic acid of the carbon numbers 2-8 of a fumaric acid, a citraconic acid, mesaconic acid, a phthalic acid, isophthalic acid, a terephthalic acid, etc., For example, with a carbon numbers [ of tricarballic acid benzene tricarboxylic acid, etc. ] of six or more tricarboxylic acid, For example, with a carbon numbers [ , such as tartronic acid and a malic acid, ] of three or more mono-hydroxy dicarboxylic acid, For example, with a carbon numbers [ , such as with a carbon numbers / of a tartaric acid etc. / of four or more dihydroxy dicarboxylic acid, for example a citric acid etc., ] of six or more mono-hydroxy tricarboxylic acid, for example, hydroxy tricarboxylic acid, such ammonium salt, etc. are mentioned. Especially, dicarboxylic acid, mono-hydroxy dicarboxylic acid, mono-hydroxy tricarboxylic acid, and dihydroxy dicarboxylic acid are desirable, and dicarboxylic acid and especially mono-hydroxy tricarboxylic acid are desirable. Oxalic acid, a malonic acid, a phthalic acid, a malic acid, a citric acid, and a tartaric acid are desirable, and, more specifically, a citric acid and especially oxalic acid are desirable. Moreover, these organic acids may be used independently, or two or more sorts, it may combine suitably and they may be used. Although the amount of the organic acid used does not generally have \*\*\*\*\* since it changes with classes of organic acid, it is 0.0001 - 20 % of the weight usually 0.05 - 10 % of the weight more preferably 0.001 to 10% of the weight.

[0049] That what is necessary is just what is usually used in this field as an amine used in this invention Although not limited especially, for example Monomethylamine, ethylamine, n propylamine, N butylamine, n-pentylamine, n-hexylamine, a cyclopentyl amine, The alkylamine of the carbon numbers 1-6, such as cyclohexylamine, for example, dimethylamine, the carbon numbers 2-12, such as a methylethyl amine, diethylamine, and a dipropyl amine, — desirable — the dialkyl amine of carbon numbers 2-6 — For example, a trimethylamine, dimethyl ethylamine, methyl diethylamine, the

carbon numbers 3-18, such as triethylamine and tripropylamine, — desirable — the alkylamine of carbon numbers 3-6 — For example, monoethanolamine, diethanolamine, triethanolamine, the carbon numbers 1-18, such as dimethylethanolamine and diethyl ethanolamine, — desirable — the monochrome of carbon numbers 1-6 thru/or trihydroxy alkylamine — For example, methylene diamine, ethylenediamine, propylenediamine, Isopropanal pyrene diamine, butylene diamine, methyl methylene diamine, Ethyl ethylenediamine, methyl ethylene diamine, methyl propylenediamine, ethyl propylenediamine and pentene diamine — passing — xylene diamine — To cyclo pentene diamine and cyclo, the alkylene diamine of the carbon numbers 1-6, such as xylene diamine, for example, the carbon numbers 2-12, such as dimethylene triamine and diethylenetriamine, — desirable — the dialkylenetriamine of carbon numbers 2-4 — for example, the carbon numbers 3-18, such as a trimethylene tetramine and triethylenetetramine, — desirable — the thoria RUKIREN tetramine of carbon numbers 3-6 — For example, tetramethylammonium hydroxide, tetraethylammonium hydroxide, Tetra-n-propyl ammonium hydroxide, tetra-n-butyl ammonium hydroxide, Tetra-n-pentyl ammonium hydroxide, tetra-n-hexyl ammonium hydroxide, (The tetra-alkylammonium hydroxide [4], for example, following general formula, of the carbon numbers 4-24, such as tetracyclo pentyl ammonium hydroxide and tetracyclo hexyl ammonium hydroxide)

[0050]

[Formula 4]

[0051] (— R3 shows an alkyl group among a formula, R4 and R5 show an alkylene group, and m and n show a positive integer.) — the alkylamine-alkylene oxide addition product shown is mentioned. In a general formula [4], as an alkyl group shown by R3 The thing of 1-4 is mentioned more preferably. for example, the thing of the shape of a straight chain, the shape of branching, and the annular usual carbon numbers 1-10 — desirable — the thing of 1-6 — specifically For example, a methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl radical, an iso-pentyl radical, a sec-pentyl radical, a tert-pentyl radical, A neopentyl radical, n-hexyl group, an iso-hexyl group, 3-methyl pentyl radical, 2-methyl pentyl radical, 1, 2-dimethyl butyl, a sec-hexyl group, A tert-hexyl group, n-heptyl radical, an

iso-heptyl radical, a sec-heptyl radical, n-octyl radical, an iso-octyl radical, a sec-octyl radical, n-nonyl radical, n-decyl group, a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, a cycloheptyl radical, a cyclo octyl radical, a cyclodecyl radical, etc. are mentioned. Especially a cyclohexyl radical etc. is desirable especially. as the alkylene group shown by R4 and R5 — the low-grade alkylene group of the shape of a straight chain, the shape of branching, and the annular carbon numbers 1-6 — desirable — for example, a methylene group, ethylene, a propylene radical, a butylene radical, a methyl methylene group, ethyl ethylene, a methyl ethylene radical, a methyl propylene radical, an ethyl propylene radical, and a pentene radical — it passes, a xylene radical etc. is mentioned to a xylene radical, a cyclo pentene radical and cyclo, and a methylene group, especially ethylene, etc. are desirable especially moreover, m and n — a positive integer — being shown — usually — 1-10 — it is 1-5 preferably. As an alkylamine-alkylene oxide addition product shown by the above-mentioned \*\*\*\* general formula [4] Specifically For example, methyl AMINJI (polyoxymethylene), methyl AMINJI (polyoxyethylene), Methyl AMINJI (polyoxy ethyl propylene), methyl AMINJI (polyoxy cyclo hexylene), Monomethylamine (polyoxymethylene) (polyoxyethylene), monomethylamine (polyoxymethylene) (polyoxy ethyl propylene), Monomethylamine (polyoxymethylene) (polyoxy cyclo hexylene), Monomethylamine (polyoxyethylene) (polyoxy ethyl propylene), Monomethylamine (polyoxyethylene) (polyoxy cyclo hexylene), Monomethylamine (polyoxy ethyl propylene) (polyoxy cyclo hexylene), Ethyl AMINJI (polyoxymethylene), ethyl AMINJI (polyoxyethylene), Ethyl AMINJI (polyoxy ethyl propylene), ethyl AMINJI (polyoxy cyclo hexylene), Ethylamine (polyoxymethylene) (polyoxyethylene), ethylamine (polyoxymethylene) (polyoxy ethyl propylene), Ethylamine (polyoxymethylene) (polyoxy cyclo hexylene), Ethylamine (polyoxyethylene) (polyoxy ethyl propylene), Ethylamine (polyoxyethylene) (polyoxy cyclo hexylene), Ethylamine (polyoxy ethyl propylene) (polyoxy cyclo hexylene), Propylure MINJI (polyoxymethylene), propylure MINJI (polyoxyethylene), Propylure MINJI (polyoxy ethyl propylene), propylure MINJI (polyoxy cyclo hexylene), Propylamine (polyoxymethylene) (polyoxyethylene), propylamine (polyoxymethylene) (polyoxy ethyl propylene), Propylamine (polyoxymethylene) (polyoxy cyclo hexylene), Propylamine (polyoxyethylene) (polyoxy ethyl propylene), Propylamine (polyoxyethylene) (polyoxy cyclo hexylene), Alkyl AMINJI, such as propylamine (polyoxy ethyl propylene) (polyoxy cyclo hexylene) (polyoxyalkylene), For example, cyclohexyl AMINJI (polyoxymethylene), cyclohexyl AMINJI (polyoxyethylene), Cyclohexyl AMINJI (polyoxypropylene), cyclohexyl AMINJI (polyoxy butylene), Cyclohexyl AMINJI (polyoxy methyl

methylene), cyclohexyl AMINJI (polyoxy ethyl ethylene), Cyclohexyl AMINJI (polyoxy ethyl propylene), cyclohexyl AMINJI (polyoxy pentene), Cyclohexyl AMINJI (it is a xylene to polyoxy), cyclohexyl AMINJI (polyoxy cyclo hexylene), Cyclohexylamine (polyoxymethylene) (polyoxyethylene), Cyclohexylamine (polyoxymethylene) (polyoxy ethyl propylene), Cyclohexylamine (polyoxymethylene) (polyoxy cyclo hexylene), Cyclohexylamine (polyoxyethylene) (polyoxy ethyl propylene), Cyclohexylamine (polyoxyethylene) (polyoxy cyclo hexylene), Cyclohexylamine (polyoxy ethyl propylene) (polyoxy cyclo hexylene), Cyclodecyl AMINJI (polyoxymethylene), cyclodecyl AMINJI (polyoxyethylene), Cyclodecyl AMINJI (polyoxy ethyl propylene), cyclodecyl AMINJI (polyoxy cyclo hexylene), A cyclodecyl amine (polyoxymethylene) (polyoxyethylene), A cyclodecyl amine (polyoxymethylene) (polyoxy ethyl propylene), A cyclodecyl amine (polyoxymethylene) (polyoxy cyclo hexylene), A cyclodecyl amine (polyoxyethylene) (polyoxy ethyl propylene), Cycloalkyl AMINJI (polyoxyalkylene), such as a cyclodecyl amine (polyoxyethylene) (polyoxy cyclo hexylene) and a cyclodecyl amine (polyoxy ethyl propylene) (polyoxy cyclo hexylene), etc. is mentioned.

[0052] Also in the above-mentioned \*\*\*\* amine, alkylene diamine, dialkylenetriamine, a thoria RUKIREN tetramine, an alkylamine-alkylene oxide addition product, and tetra-alkylammonium hydroxide are desirable, and alkylene diamine and especially cycloalkyl AMINJI (polyoxyalkylene) are desirable especially. Ethylenediamine, diethylenetriamine, triethylenetetramine, cyclohexyl AMINJI (polyoxyethylene), cyclohexylamine (polyoxyethylene) (polyoxymethylene), and tetramethylammonium hydroxide are desirable, and, specifically, ethylenediamine and especially cyclohexyl AMINJI (polyoxyethylene) are desirable especially. Moreover, these amines may be used independently, or two or more sorts, it may combine suitably and they may be used. Although the amount of the amine used does not generally have \*\*\*\*\* since it changes with classes of amine, it is 0.0001 - 20 % of the weight usually 0.05 - 10 % of the weight more preferably 0.001 to 10% of the weight.

[0053] That what is necessary is just what is usually used in this field as an inorganic alkali compound used in this invention, although not limited especially, inorganic alkali, such as nitrogen content inorganic alkali compounds, for example, a potassium hydroxide, such as a hydroxy amine, a hydrazine, ammonia, and these salts (for example, a hydrochloride, a sulfate, etc.), and a sodium hydroxide, etc. is mentioned, for example. Especially, a nitrogen content inorganic alkali compound is desirable, and the nitrogen content inorganic alkali compound which does not contain a metal especially is desirable. A hydroxylamine, a hydrazine, and ammonia are specifically desirable, and

ammonia is desirable especially. Moreover, these inorganic alkali compound may be used independently, or two or more sorts, it may combine suitably and it may be used. Although the amount of the inorganic alkali compound used does not generally have \*\*\*\*\* since it changes with classes of inorganic alkali compound, it is 0.0001 - 20 % of the weight usually 0.05 - 10 % of the weight more preferably 0.001 to 10% of the weight.

[0054] It is not limited especially that what is necessary is just what is usually used in this field as a chelating agent used in this invention. By adding a chelating agent, metallic oxides, such as copper oxide distributed in liquid, can be solubilized, and re-adsorption can be suppressed, and impurities, such as Fe and aluminum, can also be removed from a substrate front face. As such a chelating agent, for example EDTA (ethylenediaminetetraacetic acid), EDDA (ethylenediamine 2 acetic acid), EDTA-OH (hydroxy ethylenediamine triacetic acid), GEDTA (glycol ether diamine tetraacetic acid), DTPA (diethylenetriamine pentaacetic acid), IDA (iminodiacetate), methyl-EDTA (diaminopropane tetraacetic acid), NTA (nitrilotriacetic acid), TTHA (triethylenetetramine 6 acetic acid), Straight chain mold amino polycarboxylic acid, such as such ammonium salt and complex salt of these and an amine For example, CyDTA (trans-cyclohexyl diamino tetraacetic acid), Amino polycarboxylic acid, such as annular amino polycarboxylic acid, such as ammonium salt of this, and complex salt of this and an amine For example, NTPO (nitrilotrismethylene phosphonic acid), HEDPO (hydroxy ECHIRIDENJI (methylene phosphonic acid)), Pori phosphonic acid, such as such ammonium salt and complex salt of these and an amine For example, EDDPO (ethylene JIAMINJI (methylene phosphonic acid)), EDTPO (ethylenediamine tetrapod (methylene phosphonic acid)), PDTPO (diaminopropane tetrapod (methylene phosphonic acid)), Phosphonic acid, such as amino poly phosphonic acid, such as DETPPO (diethylenetriamine PENTA (methylene phosphonic acid)), TTHPO(s) (triethylenetetramine hexa (methylene phosphonic acid)), such ammonium salt, and complex salt of these and an amine, is mentioned. Especially, EDTA, CyDTA, HEDPO, EDTPO, DETPPO(s), such ammonium salt, and especially the complex salt of these and an amine are desirable. In addition, in the above, the thing same as an amine which forms complex salt as the amine described previously is mentioned. Moreover, these chelating agents may be used independently, or two or more sorts, it may combine suitably and they may be used. Although the amount of the chelating agent used does not generally have \*\*\*\*\* since it changes with classes of chelating agent, it is 0.0001 - 10 % of the weight usually 0.0001 - 0.5 % of the weight more preferably 0.0001 to 1% of the weight.



[0055] It is not limited especially that what is necessary is just what is usually used in this field as a surfactant used in this invention. By adding a surfactant, the wettability of an aqueous solution to a substrate front face can be improved. The Nonion system surfactant which has a polyoxyalkylene group, for example in a molecule as such a surfactant, For example, the anion system surfactant which has the radical chosen from a sulfonic group, a carboxyl group, a phosphonic acid radical, a sulfo KISHIRU radical, and a phosphono KISHIRU radical into a molecule, For example, quaternary ammonium, such as alkylamine, for example, alkyl trimethylammonium, and alkyl dimethylbenzyl ammonium, For example, cation system surfactants, such as alkyl pyridinium and these salts (for example, a hydrochloride, a sulfate, etc.), For example, although amphoteric surface active agents, such as an alkyl betaine derivative, an imidazolinium betaine derivative, a sulfobetaine derivative, an amino carboxylic-acid derivative, an imidazoline derivative, and an amine oxide derivative, etc. are mentioned, it is not limited to these. As an Nonion system surfactant which has a polyoxyalkylene group in a molecule Polyoxyalkylene alkyl ether, the polyoxyalkylene poly alkyl aryl ether, etc. are mentioned. For example, more specifically For example, the Nonion system surfactant which has a polyoxyethylene radical in molecules, such as polyoxyethylene alkyl ether and polyoxyethylene alkyl phenyl ether, For example, the Nonion system surfactant which has a polyoxypropylene radical in molecules, such as polyoxypropylene alkyl ether and the polyoxypropylene alkylphenyl ether, For example, the Nonion system surfactant which has a polyoxyethylene radical and a polyoxypropylene radical is mentioned into molecules, such as polyoxyethylene polyoxypropylene alkyl ether and the polyoxyethylene polyoxypropylene alkylphenyl ether. As an anion system surfactant which has the radical chosen from a sulfonic group, a carboxyl group, a phosphonic acid radical, a sulfo KISHIRU radical, and a phosphono KISHIRU radical into a molecule For example, an alkyl sulfonic acid, alkylbenzene sulfonic acid, an alkyl naphthalene sulfonic acid, These salts (for example, alkali-metal salts, for example, ammonium salt etc., such as sodium and a potassium) The anion system surfactant which has a sulfonic group in a molecule, like ammonium salt is desirable especially, For example, an alkyl carboxylic acid, an alkylbenzene carboxylic acid, an alkyl naphthalene carboxylic acid, These salts (for example, alkali-metal salts, for example, ammonium salt etc., such as sodium and a potassium) The anion system surfactant which has a carboxyl group in a molecule, like ammonium salt is desirable especially, For example, alkyl phosphonic acid, alkylbenzene phosphonic acid, alkyl naphthalene phosphonic acid, These salts (for example, alkali-metal salts, for example, ammonium salt etc., such as sodium and a potassium) The anion system surfactant

which has a phosphonic acid radical in a molecule, like ammonium salt is desirable especially. For example, alkyl-sulfuric-acid ester, an alkylbenzene sulfate, polyoxyethylene alkyl-sulfuric-acid ester, A polyoxyethylene alkylbenzene sulfate, a polyoxyethylene alkyl naphthalene sulfate, The anion system surfactant which has a sulfo KISHIRU radical is mentioned into molecules, such as these salts (for example, alkali-metal salts, for example, ammonium salt etc., such as sodium and a potassium, have desirable ammonium salt especially). Especially, the Nonion system surfactant and an anion system surfactant are desirable. Moreover, especially as a Nonion system surfactant, polyoxyalkylene alkyl ether is desirable, and what has a sulfonic group in a molecule, and especially the thing that has a sulfo KISHIRU radical in a molecule are desirable as an anion system surfactant. Especially the anion system surface active agent that has a sulfo KISHIRU radical in molecules, such as an anion system surface active agent which has a carboxyl group in molecules, such as the Nonion system surface active agent which has a polyoxyethylene radical and a polyoxypropylene radical in molecules, such as the Nonion system surface active agent which more specifically has a polyoxyethylene radical in molecules, such as polyoxyethylene alkyl ether, and polyoxyethylene polyoxypropylene alkyl ether, and alkylbenzene sulfonic acid, and polyoxyethylene alkyl-sulfuric-acid ester, is desirable. Moreover, these surfactants may be used independently, or two or more sorts, it may combine suitably and they may be used. Since the amount of the surfactant used changes with classes of surfactant, it does not generally have \*\*\*\*\*, but that the Nonion system surfactant should just be more than critical micelle concentration, if thinner than it, the rate of etching will become quick and effectiveness will fade. Moreover, surfactants other than a nonionic surfactant should just be the amounts in which the surface tension of a substrate finishing agent may be reduced. Although there is no \*\*\*\*\* generally as the concrete amount used since it changes with classes of surfactant, it is 0.0001 - 1 % of the weight usually 0.0001 - 0.05 % of the weight more preferably 0.0001 to 0.1% of the weight.

[0056] The metal corrosion inhibitor of this invention has the desirable thing which comes to contain the amino acid concerning above-mentioned \*\*\*\* this invention or its derivative, and at least 1 of the above-mentioned \*\*\*\* organic acid, an amine, an inorganic alkali compound, a chelating agent, and surfactants, and especially its thing that comes to contain the amino acid concerning above-mentioned \*\*\*\* this invention or its derivative, and a chelating agent or/and a surfactant is still more desirable.

[0057] By sticking to the metal corrosion inhibitor of this invention in the surface of metal which the amino acid which has a thiol group in the intramolecular concerning this invention contained there, or its derivative has, and forming a protective coat in the

front face concerned If the property in which oxidation and corrosion of the metal which protects a surface of metal and wins popularity out of a water solution or air can be controlled is used and the substrate front face which has the metallic-coating section on a front face is processed, using the metal corrosion inhibitor of this invention Oxidation and corrosion of the metal on the front face of a substrate concerned can be prevented, and the metal impurity on the front face of a substrate can be removed further effectively.

[0058] It comes to contain the processing agent of this invention by the \*\*\*\* density range which mentioned above reagents usually used in this field, such as the amino acid which has a thiol group in the intramolecular concerning the metal corrosion inhibitor of above-mentioned \*\*\*\* this invention, i.e., this invention, or its derivative, \*\*\*\* mentioned above, for example, an organic acid, an amine, an inorganic alkali compound, a chelating agent, and a surfactant, when requiring. In addition, if at least one of the reagents used \*\*\*\* usual at this rate [ above-mentioned ] in the fields is made to contain in the processing agent of this invention, metal impurities (for example, metallic oxides, such as oxidation copper and ferrous oxide etc.), particle, etc. can be more effectively removed to preventing oxidation and corrosion of the metal on the front face of a substrate, and coincidence. Especially the thing that comes to contain the amino acid applied to above-mentioned \*\*\*\* this invention especially or its derivative, and a chelating agent or/and a surfactant is desirable. The above-mentioned example of \*\*\*\* reagents, a desirable mode, etc. are as having stated previously.

[0059] The processing agent of this invention is usually in the condition of an aqueous solution, and is prepared by making water carry out the addition dissolution of the amino acid concerning this invention concerned, or its derivative by the same preparation approach as the metal corrosion inhibitor of \*\*\*\* this invention mentioned above.

[0060] Thus, as for the processing agent of prepared this invention, it is desirable to perform filtration processing etc. before use.

[0061] The art (the metal corrosion prevention approach) of this invention contacts the processing agent (metal corrosion inhibitor) of above-mentioned \*\*\*\* this invention, and the metal on the front face of a substrate which has the metallic-coating section on a front face, and should just process the substrate front face concerned by the processing agent (the metal corrosion prevention approach) of this invention.

[0062] the very thing usually performed in this field as an approach of processing the substrate front face which has the metallic-coating section on a front face by the processing agent (the metal corrosion prevention approach) of this invention —

specifically, approaches, such as DIP processing only immersed into a processing agent (metal corrosion inhibitor) in a substrate and sheet processing which sprinkles a processing agent over a substrate in the shape of a shower, are mentioned that what is necessary is just a well-known approach.

[0063] In this invention, as described above as "processing", it says contacting the processing agent of this invention, and the metal on the front face of a substrate. Although pretreatment before giving preservation processing, for example, washing processing etc., washing processing, etc. are more specifically mentioned, it is not limited to these.

[0064] That is, the metal corrosion inhibitor of this invention can be used also as processing agents, such as a preservative for substrates which has the metallic-coating section on a front face, a pretreatment agent for substrates which has the metallic-coating section on a front face, or a cleaning agent for substrates which has the metallic-coating section on a front face.

[0065] For example, if the processing agent of this invention is used for a front face as a preservative for substrates which has the metallic-coating section, the oxidation and corrosion in which the metal concerned receives during substrate preservation can be prevented, and the metal impurity on the front face of a substrate can also be further removed from various ambient atmospheres, such as a water solution and air, effectively. After performing the approaches of saving performing the approach of saving while \*\*\*\* DIP processing described above, for example was performed as a store method of the substrate of this invention and the substrate had been immersed into the processing agent (preservative) of this invention, the above-mentioned \*\*\*\* sheet processing, etc., and sprinkling the processing agent (preservative) of this invention over a substrate, or these processings, the method of drying and saving a substrate etc. is mentioned.

[0066] Moreover, if it uses as a pretreatment agent for the substrates concerned and the metal on the front face of a substrate is processed before \*(ing) the substrate which has the metallic-coating section for the processing agent of this invention on a front face at a washing process etc., for example The oxidation and corrosion which a metal receives into the process of degree process can be prevented, and easy actuation of washing by ultrapure water etc. can remove effectively the metal impurity on the front face of a substrate from various ambient atmospheres, such as air while water solutions and degree processes, such as a cleaning agent used at degree process, \*\*, further. After performing the approach immersed in a substrate into the processing agent (pretreatment agent) of this invention by \*\*\*\* DIP processing described above, for example as the pretreatment approach of the substrate of this invention, the approaches

of sprinkling the processing agent (pretreatment agent) of this invention over a substrate by the above-mentioned \*\*\*\* sheet processing, or these processings, the approach of drying a substrate etc. is mentioned.

[0067] thus, the very thing to which the obtained substrate is usually performed in this field — it can \*\* to the washing approach using a well-known finishing agent (cleaning agent). As a finishing agent (cleaning agent) used in the above Although all the things used in this field can be used and it is not limited especially For example, JP,5-263275,A, JP,6-112646,A, JP,6-287774,A, JP,7-54169,A, JP,7-79061,A, JP,7-166381,A, JP,7-292483,A, JP,2000-8185,A, The finishing agent (cleaning agent) indicated by JP,10-251867,A, JP,7-267933,A, JP,11-50275,A, etc., the cleaning agent of this invention mentioned later, etc. are mentioned.

[0068] Furthermore, if the substrate front face which uses the processing agent of this invention for a front face as a cleaning agent for substrates which has the metallic-coating section, for example, and has the metallic-coating section on a front face is processed, the corrosion and oxidation of the metal on the front face of a substrate can be prevented, and the metal impurity of the front face concerned can be removed effectively.

[0069] The amino acid which has a thiol group in the intramolecular concerning this invention as the processing agent of this invention was mentioned above, or its derivative, The amino acid which whose thing which comes to contain at least one of \*\*\*\* and the organic acid which were mentioned above, an amine, an inorganic alkali compound, a chelating agent, and surfactants is desirable, and requires it for this invention, or its derivative, Although the thing which comes to contain a chelating agent or/and a surfactant is more desirable, in case the processing agent of this invention is used as a cleaning agent, especially considering as such a presentation is desirable. In addition, the example of the above-mentioned \*\*\*\* organic acid, an amine, an inorganic alkali compound, a chelating agent, and a surfactant, a desirable mode, etc. are as having stated previously.

[0070] The cleaning agent of this invention is usually in the condition of an aqueous solution, and is prepared by making water carry out the addition dissolution of the amino acid concerning this invention concerned, or its this, at least 1 [ or ] of an organic acid, an amine, an inorganic alkali compound, a chelating agent, and surfactants and derivative. As an approach of dissolving the amino acid concerning this invention, or its derivative in water For example, the amino acid concerning this invention which dissolved separately into water or its derivative (or with this) The approach of adding at least one of the organic acid which dissolved separately, an amine, an inorganic alkali

compound, a chelating agent, and surfactants, the amino acid concerning this invention, or its derivative (or with this) the approach of adding at least one of an organic acid, an amine, an inorganic alkali compound, a chelating agent, and surfactants in direct water, and dissolving and stirring — or The approach of stirring and mixing at least one of the organic acid and amine which added in water separately and dissolved with the amino acid concerning this invention which added and dissolved into water, or its derivative, an inorganic alkali compound, a chelating agent, and surfactants etc. is mentioned.

[0071] Thus, as for the prepared cleaning agent of this invention, it is desirable to perform filtration processing etc. before use. Moreover, although the water used here should just be refined by distillation, ion exchange treatment, etc., the so-called ultrapure water used in this field is more desirable.

[0072] What is necessary is just to process the washing approach of this invention with the cleaning agent of \*\*\*\* this invention which described above the substrate front face which has the metallic-coating section on a front face.

[0073] the very thing usually performed in this field as an approach of processing the substrate front face which has the metallic-coating section on a front face with the cleaning agent of this invention — approaches mentioned above, such as \*\*\*\* DIP processing and sheet processing, are mentioned that what is necessary is just the well-known washing approach.

[0074] Furthermore, in this invention, metal impurities (oxidation equivalent metallic oxide etc.) can be more effectively removed by using physical washing together at the time of washing. Giving the substrate front face which has the metallic-coating section on a front face to a physical washing process under existence of the cleaning agent of this invention as the concrete approach of concomitant use etc. is mentioned.

[0075] In the above-mentioned approach, the approach of giving to a physical washing process as a condition in which the cleaning agent of this invention was made to specifically exist by the above-mentioned \*\*\*\* DIP processing, sheet processing, etc. as an approach in which the cleaning agent of this invention is made to exist etc. is mentioned. Moreover, brush scrub washing which washes a substrate front face, for example, using the brush made from polyvinyl alcohol of high-speed rotation etc. as physical washing (process), megasonic washing using a RF, etc. are mentioned.

[0076] As more concrete technique in the case of using physical washing together For example, the method of performing physical washing, after considering as the condition of having taken out the substrate out of the penetrant remover concerned after being immersed into the cleaning agent of this invention, and having made the cleaning agent concerned existing in a substrate front face, How to perform physical washing after

considering as the condition of having sprinkled the cleaning agent of this invention over the approach and substrate front face which perform physical washing while the substrate had been made immersed into the cleaning agent of this invention, and having made the cleaning agent concerned existing in a substrate front face, Or the method of performing physical washing etc. is mentioned, sprinkling the cleaning agent of this invention over a substrate front face.

[0077] Especially the acidity or alkalinity of the metal corrosion inhibitor of above-mentioned \*\*\*\* this invention and processing agents (a preservative, a pretreatment agent, cleaning agent, etc.) is not limited, but is suitably chosen from pH range usually used in this field by a class, the purpose, etc. of using the substrate used. more — concrete — the acescence thru/or alkalinity — desirable — usually — pH 2-13 — desirable — pH 3-12 — it is pH 4-10 more preferably. By considering as such pH range, since electric repulsion with a substrate front face and particle becomes large, the removal effectiveness of particle and metal impurities (for example, metallic oxides, such as copper oxide etc.) improves, and a possibility of etching SiO<sub>2</sub> which is an interlayer insulation film further decreases more.

[0078] The metal corrosion inhibitor and the processing agents of this invention (a preservative, a pretreatment agent, cleaning agent, etc.) can be used for the substrate which has the metallic-coating section on a front face. As such a substrate, the glass substrate used, for example for printed circuit boards, such as a semi-conductor substrate and polyimide resin, LCD, etc. is mentioned, and it is useful to especially a semi-conductor substrate. Moreover, copper, chromium, silver, gold, etc. are mentioned and it is [ that what is necessary is just sulfur and the metal which reacts as a metal covered by the substrate front face concerned ] useful in especially metal copper. Especially, it is useful to especially the semi-conductor substrate that has the copper covering section on a front face (copper wiring was given).

[0079] Although an example and the example of a comparison are given to below, this invention is not limited at all by these.

[0080] Moreover, the amount of adsorption (residual Cu concentration) of Cu (copper atom) which the metal Cu deposition wafer and Cu contamination wafer which were used in this example and the example of a comparison use what was prepared by the following approaches, respectively, and is carrying out adsorption survival on the thickness of Cu of a metal Cu deposition wafer front face and Cu contamination wafer front face was measured by the following approaches, respectively.

[0081] [Metal Cu deposition wafer] The thing which made Metal Cu deposit on the front face of a 4 inch silicon wafer by the spatter was used as the copper deposition

wafer. In addition, the thickness of the copper of the metal Cu deposition wafer front face concerned checked that it was 1000nm by the approach shown below.

[0082] [Cu contamination wafer] — for [ slurry water-solution / which added Cu ion so that the 4 inch silicon wafer which set the front face to SiO<sub>2</sub> by the oxidizing / thermally / method might be set to 1 ppm / (0.1% hydrogen peroxide solution of 1% silica content) ] 1L1 minute — being immersed — ultrapure water — for 10 minutes — a stream — after washing, what carried out spin desiccation was used as Cu contamination wafer. In addition, to the Cu contamination wafer concerned, it checked that Cu (copper atom) was carrying out  $3 \times 10^{14}$  atom / cm<sup>2</sup> adsorption survival by the approach shown below.

[0083] [Metal Cu thickness measurement method] The wafer was divided into one half, the cross section was observed with the electron microscope, and metal Cu thickness was measured.

[0084] [Cu density measurement method] On the wafer front face, after carrying out dissolution recovery of the Cu which carried out adsorption survival in a fluoric acid-nitric-acid water solution, Cu concentration in this recovery liquid was measured with the atomic absorption method (graphite furnace atomic-absorption-analysis equipment). Based on the obtained measured value, the amount of adsorption (residual Cu concentration) of Cu (copper atom) was calculated.

[0085] In addition, in this example and the example of a comparison, all especially of % which expresses concentration as long as there is no notice, and ppm and ppb show a weight ratio. Moreover, all the water to be used was ultrapure water, and it was used after checking that copper was 0.01 or less ppb.

[0086]

[Example] The metal Cu deposition wafer produced by the above-mentioned approach was immersed in each metal corrosion inhibitor (preservative) 1L given in one to example 14 table 1 under the room temperature for 5 hours. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Thus, in order to observe the color tone of Cu film front face on the front face of a wafer visually in order to check the existence of oxidation of Metal Cu, and to check the existence of the corrosion of Metal Cu about the processed metal Cu deposition wafer, the thickness of the metal Cu on the front face of a wafer was measured. A result is shown in Table 1.

[0087]

[Table 1]



	金属腐蝕防止剤 (濃度：重量%)	Cu膜表面の 色調	Cu膜厚 (nm)
実施例1	システイン(0.05)	変化なし	940
実施例2	システインメチルエステル (0.001)	変化なし	950
実施例3	システインエチルエステル (0.001)	変化なし	980
実施例4	ホモシステイン(0.001)	変化なし	1000
実施例5	システイン(0.01) シュウ酸(0.3)	変化なし	1000
実施例6	システイン(0.001) エチレンジアミン(0.001)	変化なし	980
実施例7	アセチルシステイン(0.05) アンモニア(0.1)	変化なし	950
実施例8	アセチルシステイン(0.01) EDTA(0.001)	変化なし	1000
実施例9	システイン(0.1) TTHPO(0.01)	変化なし	970
実施例10	システイン(0.001) ポリオキシエチレンアルキルエー テル(アルキル C=8~12)(0.0001)	変化なし	950
実施例11	システイン(0.01) アルキルナフタレンカルボン酸 (0.0001)	変化なし	1000
実施例12	システイン(0.01) ヒドロキシルアミン(0.005) EDTPO(0.05)	変化なし	940
実施例13	システイン(0.01) シュウ酸(0.5) CyDTA(0.001) ポリオキシエチレンアルキル硫酸 エステル(0.01)	変化なし	960
実施例14	アセチルシステイン(0.001) クエン酸(1.0) HEDPO(0.05) アル キルスルホン酸(0.0001)	変化なし	980

[0088] Except having used the various solutions of a publication for one to example of comparison 6 table 2, after processing a metal Cu deposition wafer by the same approach as examples 1-14, the color tone of Cu film front face on the front face of a wafer was observed visually, and the thickness of the metal Cu on the front face of a wafer was measured. A result is shown in Table 2. In addition, - in Table 2 shows measurement impossible.

[0089]

[Table 2]

	溶液 (濃度：重量%)	Cu膜表面の 色調	Cu膜厚 (nm)
比較例1	水	光沢消失	—
比較例2	シュウ酸(0.01)	光沢消失	330
比較例3	アンモニア(0.01)	Cu膜溶解	0
比較例4	NH <sub>4</sub> PO <sub>4</sub> (1.0)	変化なし	550
比較例5	ポリオキシエチレンアルキルベンゼン硫酸エステル(0.1)	光沢消失	—
比較例6	クエン酸(1.0) IDA(0.05) ポリオキシプロピレンアルキル エーテル(0.01)	変化なし	770

[0090] When a metal Cu deposition wafer is saved in the metal corrosion inhibitor (preservative) (examples 1-14) of this invention so that clearly from Table 1 and 2, it is changeless to the color tone of Cu film front face on the front face of a wafer, and Metal Cu does not oxidize, and there is almost no change in Cu thickness, and it turns out that Metal Cu is not being corroded. On the other hand, when a metal Cu deposition wafer is saved in the solution of the examples 1 and 5 of a comparison, Metal Cu is corroded remarkably, and the gloss of Cu film front face on the front face of a wafer disappears, and it turns out that Metal Cu has oxidized. Moreover, although it is changeless to the color tone of Cu film front face on the front face of a wafer and Metal Cu has not oxidized when saved in the solution of the examples 4 and 6 of a comparison, Cu thickness decreases and it turns out that Metal Cu is being corroded (dissolution). Furthermore, it turns out that Metal Cu is being altogether corroded for setting for the example 2 of a comparison, and Metal Cu being oxidized and corroded (dissolution) especially in the example 3 of a comparison (dissolution). That is, the metal corrosion inhibitor of this invention can prevent metal oxidation and corrosion, if the substrate which has the metallic-coating section is saved on a front face in the processing agent (preservative) which comes to contain the metal inhibitor of this invention, oxidation and corrosion of the metal concerned can be prevented to coincidence, and it turns out that the substrate which has the metallic-coating section can be saved good in a solution on a front face.

[0091] The metal Cu deposition wafer produced by the above-mentioned approach was immersed in each metal corrosion inhibitor (preservative) 1L given in 15 to example 17 table 3 for 1 minute under the room temperature. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Subsequently, the wafer was left in air for 10 hours. Thus, in order to check the existence of oxidation of Metal Cu about the processed metal Cu deposition wafer,

the color tone of Cu film front face on the front face of a wafer was observed visually. A result is shown in Table 3.

[0092] Except having used the various solutions of a publication for seven to example of comparison 10 table 3, after processing a metal Cu deposition wafer by the same approach as examples 15-17, the color tone of Cu film front face on the front face of a wafer was observed visually. A result is combined with examples 15-17, and is shown in Table 3.

[0093]

[Table 3]

	金属腐蝕防止剤又は溶液 (濃度：重量%)	Cu膜表面の 色調
実施例15	システイン(0.05)	変化なし
実施例16	システイン(0.01) マロン酸(0.3) DETPO(0.005)	変化なし
実施例17	システイン(0.001) エチレンジアミン(0.1) PDTPO(0.05) ポリオキシエチレンポリオキシブ ロピレンアルキルエーテル (0.002)	変化なし
比較例7	水	光沢消失
比較例8	シュウ酸(0.3)	光沢消失
比較例9	アンモニア(0.01)	光沢消失
比較例10	マロン酸(0.5) EDDPO(0.01) アルキルナフタレンカルボン酸 (0.001)	光沢消失

[0094] When the wafer concerned is saved in air after processing a metal Cu deposition wafer with the metal corrosion inhibitor (preservative) (examples 15-17) of this invention so that clearly from Table 3, it is changeless to the color tone of Cu film front face on the front face of a wafer, and it turns out that Metal Cu has not oxidized. On the other hand, when a metal Cu deposition wafer is processed with the solution of the examples 7-10 of a comparison, the gloss of Cu film front face on the front face of a wafer disappears, and it turns out that Metal Cu has oxidized. That is, it turns out that the substrate which can prevent oxidation of the metal on the front face of a substrate concerned, and has the metallic-coating section on a front face by the processing agent (preservative) which comes to contain the metal inhibitor of this invention if this is saved after processing the substrate which has the metallic-coating section on a front face can be saved good in air.

[0095] 18 to example 20 table 4 was sprinkled having metal covered [ of the publication / each / 500ml ] it over the metal Cu deposition wafer front face produced by the

above-mentioned approach for 1 minute (preservative). Then, with ultrapure water, the rinse of the wafer was carried out for 10 minutes, and it carried out spin desiccation. Subsequently, the wafer was left in air for 10 hours. Thus, in order to check the existence of oxidation of Metal Cu about the processed metal Cu deposition wafer, the color tone of Cu film front face on the front face of a wafer was observed visually. A result is shown in Table 4.

[0096] Except having used the various solutions of a publication for 11 to example of comparison 14 table 4, after processing a metal Cu deposition wafer by the same approach as examples 18-20, the color tone of Cu film front face on the front face of a wafer was observed visually. A result is combined with examples 18-20, and is shown in Table 4.

[0097]

[Table 4]

	金属腐蝕防止剤又は溶液 (濃度：重量%)	Cu膜表面の 色調
実施例18	システイン(0.05)	変化なし
実施例19	アセチルシステイン(0.01) 酒石酸(0.1) EDTA-OH(0.01) ポリオキシエチレンアルキルベン ゼン硫酸エステル(0.05)	変化なし
実施例20	システイン(0.1) シクロヘキシルアミン(0.1) TTHA(0.005)	変化なし
比較例11	水	光沢消失
比較例12	シュウ酸(0.3)	光沢消失
比較例13	アンモニア(0.01)	光沢消失
比較例14	リンゴ酸(0.2) DETPPO(0.01) アルキルベンゼンスルホン酸 (0.001)	光沢消失

[0098] When the wafer concerned is saved in air after processing a metal Cu deposition wafer with the metal corrosion inhibitor (preservative) (examples 18-20) of this invention so that clearly from Table 4, it is changeless to the color tone of Cu film front face on the front face of a wafer, and it turns out that Metal Cu has not oxidized. On the other hand, when a metal Cu deposition wafer is processed with the solution of the examples 15-17 of a comparison, the gloss of Cu film front face on the front face of a wafer disappears, and it turns out that Metal Cu has oxidized. By namely, the processing agent (preservative) which comes to contain the metal inhibitor of this invention not only by the \*\*\*\*\* DIP processing performed in the examples 15-17 but by the

so-called sheet processing which was performed in the examples 18-20 If this is saved after processing the substrate which has the metallic-coating section on a front face, oxidation of the metal on the front face of a substrate concerned can be prevented, and it turns out that the substrate which has the metallic-coating section can be saved good in air on a front face.

[0099] Cu contamination wafer and the metal Cu deposition wafer which were produced by the above-mentioned approach were immersed in each metal corrosion inhibitor (pretreatment agent) 1L given in 21 to example 34 table 5 under the room temperature for 1 hour. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Subsequently, the wafer concerned was immersed in each penetrant remover 1L given in Table 5 for 10 minutes under the room temperature. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Thus, about processed Cu contamination wafer, in order to measure the residual Cu concentration which is carrying out adsorption survival on a wafer front face in order to evaluate metal impurity removal capacity, and to check the existence of oxidation of Metal Cu about a metal Cu deposition wafer, the color tone of Cu film front face on the front face of a wafer was observed visually, and further, in order to check the existence of the corrosion of Metal Cu, the thickness of the metal Cu on the front face of a wafer measured. A result is shown in Table 5. In addition, - in Table 5 shows measurement impossible.

[0100] Except having used the various solutions and each cleaning agent of a publication for 15 to example of comparison 25 table 6 After processing Cu contamination wafer and a metal Cu deposition wafer by the same approach as examples 21-34, about Cu contamination wafer The residual Cu concentration which is carrying out adsorption survival was measured on the wafer front face, and about the metal Cu deposition wafer, the color tone of Cu film front face on the front face of a wafer was observed visually, and the thickness of the metal Cu on the front face of a wafer was measured further. A result is shown in Table 6. In addition, in the examples 15-18 of a comparison, processing with metal corrosion inhibitor (pretreatment agent) was not performed, but the thing which the wafer was taken [ thing ] out to it, and the rinse was carried out [ thing ] to it for 10 minutes with ultrapure water, and made it carry out spin desiccation after the wafer concerned was immersed in each penetrant remover 1L given in Table 6 for 10 minutes under a room temperature was measured and observed.

[0101]

[Table 5]

	金属腐蝕防止剤 (濃度：重量%)	洗浄剤 (濃度：重量%)	残存Cu濃度 (Cu原子/cm <sup>2</sup> )	Cu膜表面の 色調	Cu膜厚 (nm)
実施例21	システイン(0.01)	クエン酸(10.0) HEDPO(0.5)	$2 \times 10^{10}$	変化なし	1000
実施例22	アセチルシステイン(0.01) クエン酸(1.0)	アルキルナフタレンスルホン酸アンモニウム(0.01)	$1 \times 10^{10}$	変化なし	1000
実施例23	アセチルシステイン(0.1) アンモニア(1.0)	トリエチレンテトラミン (0.05) シクロヘキシルアミンジ (ポリオキシエチレン) (0.001)	$8 \times 10^9$	変化なし	970
実施例24	システイン(0.01) シュウ酸(0.3)	クエン酸(3.0)	$8 \times 10^{10}$	変化なし	1000
実施例25		リンゴ酸(0.5) DETPPO(0.002)	$6 \times 10^{10}$	変化なし	1000
実施例26		シュウ酸(0.5) アルキルスルホン酸(0.001)	$8 \times 10^{10}$	変化なし	920
実施例27		クエン酸(10.0) HEDPO(0.5) アルキルナフタレンスルホン酸アンモニウム(0.01)	$5 \times 10^9$ 以下	変化なし	1000
実施例28		ジエチレントリアミン(1.0)	$9 \times 10^9$	変化なし	920
実施例29		TMAH(0.005) GEDTA(0.05)	$8 \times 10^{10}$	変化なし	1000
実施例30		トリエチレンテトラミン (0.05) シクロヘキシルアミンジ (ポリオキシエチレン) (0.001)	$5 \times 10^{10}$	変化なし	980
実施例31		水	$3 \times 10^{11}$	変化なし	1000
実施例32		NaOH(1.0)	$5 \times 10^{11}$	変化なし	1000
実施例33		EDTA(0.01)	$7 \times 10^{10}$	変化なし	1000
実施例34		ポリオキシエチレンノニル エーテル(0.01)	$5 \times 10^{11}$	変化なし	1000

[0102]

[Table 6]

	溶液 (濃度：重量%)	洗浄剤 (濃度：重量%)	残存Cu濃度 (Cu原子/cm <sup>2</sup> )	Cu膜表面の 色調	Cu膜厚 (nm)
比較例15	—	NaOH(1.0)	$7 \times 10^{13}$	変化なし	1000
比較例16		ポリオキシエチレンノニル エーテル(0.01)	$5 \times 10^{13}$	変化なし	1000
比較例17		シュウ酸(0.5) アルキルスルホン酸(0.001)	$5 \times 10^{13}$	変化なし	850
比較例18		ジエチレントリアミン(1.0)	$8 \times 10^{10}$	表面荒れ	450
比較例19	ベンゾトリアゾール(0.01)	クエン酸(10.0) HEDPO(0.5)	$2 \times 10^{10}$	表面荒れ	680
比較例20	ベンゾトリアゾール(0.5)	アルキルナフタレンスルホ ン酸アンモニウム(0.01)	$5 \times 10^{13}$	変化なし	1000
比較例21	イミダゾール(0.5)	トリエチレンテトラミン (0.05)	$8 \times 10^9$	光沢消失	300
比較例22	3-アミノトリアゾール(0.05) アンモニア(1.0)	シクロヘキシルアミンジ (ポリオキシエチレン) (0.001)	$9 \times 10^9$	溶解	0
比較例23	キナリジン酸(0.5) クエン酸(1.0)	クエン酸(10.0) HEDPO(0.5) アルキルナフタレンスルホ ン酸アンモニウム(0.01)	$4 \times 10^{11}$	光沢消失	800
比較例24	3-アミノ-5-メルカプトトリ アゾール(0.1) クエン酸(1.0)		$7 \times 10^{13}$	変化なし	1000
比較例25	2-メルカプトエタノール (0.01) クエン酸(1.0)		$8 \times 10^{13}$	変化なし	1000

[0103] When it pretreats using the metal corrosion inhibitor (pretreatment agent) of examples 21, 22, and 27 so that clearly from the result of Table 5 and 6, it turns out that the residual Cu concentration of Cu contamination wafer front face can be controlled for 1010 or less \*\*\*\*\*, and corrosion can be prevented in the oxidation list of Metal Cu. On the other hand, although residual Cu concentration can be controlled to the same extent, oxidation and corrosion of Metal Cu are produced or the oxidation corrosion of (the examples 19 and 23 of a comparison) and Metal Cu is suppressed when it pretreats using conventional metal corrosion inhibitor (finishing agent), residual Cu concentration is high and what (examples 20, 24, and 25 of a comparison) copper oxide cannot be effectively removed for is understood. The examples 21 and 22 of a comparison are understood that Cu film on the front face of a substrate is being corroded remarkably to the ability to remove copper oxide effectively and prevent corrosion in the oxidation list of Metal Cu in examples 23 and 30, similarly. Moreover, it also turns out that it compares when not performing this, and the oxidation and corrosion of Metal Cu at the time of washing can be controlled, and copper oxide can also be further removed from the result of examples 26, 28, 32, and 34 and the examples

15-18 of a comparison effectively if it pretreats using the metal corrosion inhibitor (pretreatment agent) of this invention. If the metal corrosion inhibitor (pretreatment agent) of this invention is used and the substrate concerned is pretreated before giving the substrate which has the metallic-coating section on a front face to a washing process so that clearly from the above thing, it can prevent that a metal receives oxidation and corrosion in a washing process, and it turns out further that a metallic oxide can also be removed effectively.

[0104] Cu contamination wafer produced by the above-mentioned approach was immersed in each cleaning agent (metal corrosion inhibitor) 1L given in 35 to example 44 table 7 for 10 minutes under the room temperature. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Moreover, the metal Cu deposition wafer produced by the above-mentioned approach was immersed in each cleaning agent (metal corrosion inhibitor) 1L given in Table 7 under the room temperature for 5 hours. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Thus, about processed Cu contamination wafer, in order to measure the residual Cu concentration which is carrying out adsorption survival on a wafer front face in order to evaluate metal impurity removal capacity, and to check the existence of oxidation of Metal Cu about a metal Cu deposition wafer, the color tone of Cu film front face on the front face of a wafer was observed visually, and further, in order to check the existence of the corrosion of Metal Cu, the thickness of the metal Cu on the front face of a wafer measured. A result is shown in Table 7.

[0105] Except having used each cleaning agent of a publication for 26 to example of comparison 37 table 8, after processing Cu contamination wafer and a metal Cu deposition wafer by the same approach as examples 35-44, the residual Cu concentration which is carrying out adsorption survival was measured on the wafer front face, and about the metal Cu deposition wafer, the color tone of Cu film front face on the front face of a wafer was observed visually, and the thickness of the metal Cu on the front face of a wafer was measured further. A result is shown in Table 8. In addition, - in Table 8 shows measurement impossible.

[0106]

[Table 7]



	洗浄剤 (濃度：重量%)	残存Cu濃度 (Cu原子/cm <sup>2</sup> )	Cu膜表面の 色調	Cu膜厚 (nm)
実施例35	システイン(0.1) シュウ酸(1.0)	$5 \times 10^{10}$	変化なし	980
実施例36	アセチルシステイン(0.001) 酒石酸(0.1) EDTA(0.001)	$2 \times 10^{10}$	変化なし	960
実施例37	システイン(0.001) リンゴ酸(0.5) NTA(0.005)	$8 \times 10^{10}$	変化なし	950
実施例38	アセチルシステイン(0.001) マロン酸(0.05) ETDPO(0.0001)	$9 \times 10^9$	変化なし	900
実施例39	システイン(0.001) クエン酸(3.0) HEDPO(0.5) ドデシルベンゼンスルホン酸(0.001)	$5 \times 10^9$ 以下	変化なし	1000
実施例40	システイン(0.01) シュウ酸(0.05) DETPO(0.001) ポリオキシエチレンポリオキシプロピレンアルキルエーテル(0.001)	$5 \times 10^9$ 以下	変化なし	1000
実施例41	アセチルシステイン(0.01) リンゴ酸(0.05) ポリオキシエチレンドデシル硫酸エステル(0.0001)	$5 \times 10^9$ 以下	変化なし	1000
実施例42	L-システイン(0.01) ヒドロキシルアミン(0.01)	$1 \times 10^{10}$	変化なし	980
実施例43	D-システイン(0.02) シクロヘキシルアミンジ(ポリオキシエチレン)(2.0)	$3 \times 10^{10}$	変化なし	1000
実施例44	システイン(0.001) トリエチレントトラミン(0.2) ポリオキシエチレンノニルフェニルエーテル(0.01)	$4 \times 10^{10}$	変化なし	930

[0107]

[Table 8]

	洗浄剤 (濃度：重量%)	残存Cu濃度 (Cu原子/cm <sup>2</sup> )	Cu膜表面の 色調	Cu膜厚 (nm)
比較例26	水	$1 \times 10^{14}$	光沢消失	—
比較例27	シュウ酸(0.3)	$5 \times 10^{10}$	光沢消失	300
比較例28	リンゴ酸(0.05) ベンゾトリアゾール(0.01)	$7 \times 10^{11}$	表面荒れ	450
比較例29	シュウ酸(0.05) ベンゾトリアゾール(0.8)	$9 \times 10^{13}$	変化なし	850
比較例30	クエン酸(1.0) EDTA(0.001) ドデシルベンゼンスルホン酸(0.001)	$1 \times 10^{10}$	光沢消失	700
比較例31	ジエチレントリアミン(0.7)	$5 \times 10^{10}$	光沢消失	300
比較例32	ポリオキシエチレンアルキルエーテル (アルキル C=8~12)(0.01)	$8 \times 10^{13}$	光沢消失	—
比較例33	ヒドロキシシラミン(0.3) ポリオキシプロピレンアルキルエーテル (0.001)	$9 \times 10^{10}$	光沢消失	700
比較例34	アンモニア(1.0) NTA(0.01)	$9 \times 10^{10}$	溶解	0
比較例35	トリアゾール(0.01)	$8 \times 10^{13}$	変化なし	1000
比較例36	2-メルカプトイミダゾリン(0.001) クエン酸(1.0)	$9 \times 10^{13}$	変化なし	1000
比較例37	チオグリセロール(0.001) エチレンジアミン(0.1)	$5 \times 10^{13}$	変化なし	1000

[0108] When a wafer is washed using the cleaning agent (metal corrosion inhibitor) (examples 35-44) of this invention so that clearly from Table 7 and 8, the residual Cu concentration on the front face of a wafer can be controlled for 1010 or less \*\*\*\*\*s, and it is changeless to the color tone of Cu film front face, and Metal Cu does not oxidize, and there is almost no change in Cu thickness, and it turns out that Metal Cu is not being corroded. On the other hand, although residual Cu concentration can be controlled for 1010 or less \*\*\*\*\*s when the cleaning agent of the examples 27, 30, 31, 33, and 34 of a comparison is used, Metal Cu oxidizes and it turns out that Metal Cu is being corroded remarkably. Moreover, although the metal Cu on the front face of a wafer does not oxidize and corrosion is hardly carried out for Metal Cu, either, when the example 29 of a comparison and the cleaning agent of 35-37 are used, residual Cu concentration is high and it turns out that the copper oxide on the front face of a wafer cannot fully be removed. Furthermore, when the cleaning agent of the examples 26 and 32 of a comparison is used, Metal Cu corrodes and oxidizes, and residual Cu concentration is high, and it turns out that the copper oxide on the front face of a wafer cannot fully be removed. When the cleaning agent of the example 28 of a comparison is

used, it turns out that Metal Cu is being corroded remarkably and the copper oxide on the front face of a wafer cannot fully be removed. That is, if the substrate front face which has the metallic-coating section on a front face using the cleaning agent of this invention is washed, it turns out that oxidation and corrosion of the metal concerned can be prevented and the metal impurity (copper oxide) of the front face concerned can be removed effectively.

[0109]

[Effect of the Invention] Metal corrosion inhibitor with safety high [ that this invention has a good metallic corrosion prevention operation like the above ], And the art of the substrate concerned which can prevent the oxidation and corrosion of copper wiring in the substrate front face and the substrate front face on which copper wiring was especially given to the front face using this, If a list is provided with the washing approach of a substrate that the corrosion and oxidation of copper wiring on the front face of a substrate concerned can be prevented, and the metal impurity (copper oxide) of the front face concerned can be removed effectively and the metal corrosion inhibitor of this invention is used for it, many problems at the time of semi-conductor manufacture are solvable, for example.

## **TECHNICAL FIELD**

[Field of the Invention] This invention relates to the cleaning agent and the washing approach on metal corrosion inhibitor and the substrate front face which used this, and the front face of a substrate where copper wiring was especially given to the front face.

## **PRIOR ART**

[Description of the Prior Art] In recent years, detailed-ization is progressing with high integration and the structure of LSI is the multilayer structure which metal wiring etc. put on the semi-conductor front face in many steps. Moreover, modification in copper with more low electric resistance (Cu) from the aluminum of the former [ wiring / which is used ] is proposed.

[0003] The so-called chemical physical polish technique (Cu-CMP) which grinds and carries out flattening of the semi-conductor substrate physically is used for the process which manufactures the semi-conductor which has the multilayer structure by which copper wiring was continued and given to the multilayer on the front face, oxidizing Metal Cu.

[0004] On the other hand, the insulator layer (silicon oxide) which isolates Cu wiring and each Cu wiring is in the unreserved condition, and the wafer front face after a

Cu-CMP process is polluted with a lot of metal impurities by the semi-conductor front face after a Cu-CMP process. It originates in adsorbing on an insulator layer and Cu shaved off by CMP remaining as a metallic oxide (copper oxide), as for metal impurity contamination.

[0005] Thus, if a metallic oxide (copper oxide) remains on an insulator layer, a copper element is spread in an insulator layer in heat treatment at a back process, the property of a device deteriorates because insulation falls, and a device will be destroyed in order for isolated wiring to raise connection, i.e., short-circuit, when contamination is remarkable. Therefore, before progressing to degree process, it is necessary to remove a metallic oxide (copper oxide).

[0006] In order to remove the above-mentioned \*\*\*\* metal impurity by the above reason, the washing process after a Cu-CMP process is indispensable.

[0007] On the other hand, the metal copper on the front face of a semi-conductor will have high activity, and by few oxidizing power, it is corroded easily, and wiring resistance will increase or it will cause an open circuit. For this reason, in the washing process after a Cu-CMP process, if the penetrant remover which uses as a principal component inorganic acids used as a penetrant remover for semi-conductors, such as a hydrochloric acid, fluoric acid, etc. with comparatively strong oxidizing power, is used conventionally, since not only copper oxide but the metal copper of wiring which adhered on the insulator layer will be dissolved, use of the acid penetrant remover concerned is not desirable. Moreover, although the cleaning agent of a copper solvent action which uses organic acids with comparatively weak oxidizing power, such as oxalic acid and a citric acid, as a principal component is also weak compared with an inorganic acid, since it had the copper solvent action, the low-concentration organic acid needed to be used as much as possible. For this reason, since the solvent power of a metallic oxide also declined when an organic acid is used by low concentration, the semi-conductor front face needed to be washed [ long duration ].

[0008] In order to cancel such a fault, it is known by adding various metal corrosion inhibitor to a cleaning agent that the corrosion of the metal copper on a semi-conductor front face can be prevented.

[0009] For example, the aromatic series system compound which makes benzotriazols and imidazole derivatives representation is indicated by JP,7-79061,A. However, the copper corrosion prevention effectiveness of these compounds is low, and the prevention effectiveness is accepted only by high concentration. However, the compound concerned had the low solubility to water, and it was difficult to add these compounds by high concentration in the ultrapure water generally used as a diluent in

case the cleaning agent for semi-conductors is used. Moreover, in order to have used these compounds by high concentration, alkali solubilizing agents, such as an amine, the organic solvent of an alcoholic system, etc. were needed, but these solubilizing agents and an organic solvent were difficult to use it in order to have a bad influence on a washing property.

[0010] Moreover, ring compounds, such as mercaptoimidazole and a mercapto thiazole, are indicated by JP,2000-87268,A and JP,2000-282096,A. However, if it combines with the copper on the front face of a semi-conductor, since a copper front face will serve as hydrophobicity and these compounds will prevent the attack of a cleaning agent, it becomes difficult to remove these compounds. Thus, while the organic substance like these compounds had remained on the copper front face, when the semi-conductor received heat treatment in a next process, the time of device actuation, etc., the organic substance concerned carried out combustion, explosion, etc., and there was a problem in the problem that a serious defect will arise, safety [ as opposed to / toxicity is strong and / the body or an environment ], etc.

[0011] Furthermore, the fatty alcohol system compound which the carbon which had the sulfhydryl group in molecules, such as mercaptoethanol and mercapto glycerol, and the sulfhydryl group concerned has combined with JP,2000-273663,A, and the carbon which the hydroxyl group has combined have adjoined and combined is indicated. However, although a possibility of having effect harmful to people's health and ecosystem compared with the conventional thing is made for the purpose of offering little metal corrosion inhibitor from the problem about effect, environmental pollution, etc. in recent years to the body, invention indicated by JP,2000-273663,A A problem is still in safety, and these compounds have an unpleasant smell, even when it is added and used into a water solution, and toxicity is strong and they are not [ vapor pressure is comparatively low and ] practical.

## **EFFECT OF THE INVENTION**

[Effect of the Invention] Metal corrosion inhibitor with safety high [ that this invention has a good metallic corrosion prevention operation like the above ], And the art of the substrate concerned which can prevent the oxidation and corrosion of copper wiring in the substrate front face and the substrate front face on which copper wiring was especially given to the front face using this, If a list is provided with the washing approach of a substrate that the corrosion and oxidation of copper wiring on the front face of a substrate concerned can be prevented, and the metal impurity (copper oxide) of the front face concerned can be removed effectively and the metal corrosion inhibitor of

this invention is used for it, many problems at the time of semi-conductor manufacture are solvable, for example.

### **TECHNICAL PROBLEM**

[Problem(s) to be Solved by the Invention] This invention is what was made in view of the above-mentioned \*\*\*\* situation. Metal corrosion inhibitor with safety high [ having a good metallic corrosion prevention operation ], And the art of the substrate concerned which can prevent the oxidation and corrosion of copper wiring in the substrate front face and the substrate front face on which copper wiring was especially given to the front face using this, The washing approach of a substrate that the corrosion and oxidation of copper wiring on the front face of a substrate concerned can be prevented in a list, and the metal impurity (copper oxide) of the front face concerned can be effectively removed in it is offered.

### **MEANS**

[Means for Solving the Problem] This invention consists of the following configurations.

[0014] (1) Metal corrosion inhibitor which comes to contain in intramolecular the amino acid which has a thiol group, or its derivative.

[0015] (2) The processing agent which comes to contain the metal corrosion inhibitor of a publication in the above (1).

[0016] (3) The art of this substrate characterized by processing a substrate by the processing agent of a publication to the above (2).

[0017] (4) The cleaning agent which comes to contain the metal corrosion inhibitor of a publication in the above (1).

[0018] (5) The washing approach of this substrate characterized by washing with a cleaning agent given [ a substrate ] in the above (4).

[0019] (6) The art of this substrate characterized by processing the substrate concerned by the processing agent of a publication to the above (2) after giving the semi-conductor substrate which has the copper covering section on a front face to chemical physical polish processing (CMP).

[0020] (7) The art of this substrate characterized by processing the substrate concerned by the processing agent of a publication to the above (2), and subsequently washing the substrate concerned with a semi-conductor substrate cleaning agent after giving the semi-conductor substrate which has the copper covering section on a front face to chemical physical polish processing (CMP).

[0021] (8) The washing approach of this substrate characterized by washing with a

cleaning agent given [ the substrate concerned ] in the above (4) after giving the semi-conductor substrate which has the copper covering section on a front face to chemical physical polish processing (CMP).

[0022] Safety is [ whose amino acid which has a thiol group in intramolecular or its derivative has a good metallic corrosion prevention operation as a result of repeating research wholeheartedly that this invention person etc. should attain the above-mentioned purpose ] high, If a substrate is processed using the cleaning agent containing amino acid or its derivative concerned in a list The corrosion or oxidation of copper wiring are not caused for a substrate front face and the substrate front face where copper wiring was especially given to the front face, but it came to complete a header and this invention for the ability of the metal impurity (copper oxide) of the front face concerned to be removed effectively.

[0023] The amino acid (it may be hereafter written as the amino acid concerning this invention) which has a thiol group in the intramolecular concerning this invention has a thiol group, a carboxyl group, and an amino group in intramolecular, and the compound specifically shown by the following general formula [1] is mentioned.

[0024]

[Formula 1]

[0025] (R shows a low-grade alkylene group among a formula.)

[0026] as the low-grade alkylene group shown by R in a general formula [1] — a methylene group, ethylene, a trimethylene radical, a tetramethylen radical, a pentamethylene radical, a hexamethylene radical, a propylene radical, a butylene radical, a methyl methylene group, ethyl ethylene, a methyl ethylene radical, a methyl propylene radical, an ethyl propylene radical, and a pentene radical — it passes and the low-grade alkylene group of the shape of a straight chain, such as a xylene radical the shape of branching, and the annular carbon numbers 1-6 be mentioned to a xylene radical, a cyclo pentene radical, and cyclo. Especially, the alkylene group (a methylene group, ethylene, a trimethylene radical, a tetramethylen radical, a pentamethylene radical, hexamethylene radical) of the shape of a straight chain of carbon numbers 1-6 is desirable, and a methylene group or especially ethylene is desirable.

[0027] the amino acid which has a thiol group in the intramolecular concerning this invention — a commercial item (for example, product made from Wako Pure Chem Industry) — you may use — the very thing — according to a well-known approach, it may

prepare suitably and you may use.

[0028] As a compound shown by the above-mentioned general formula [1], a cysteine, a homocysteine, etc. are mentioned and, as for these, even the mixture of D object from which a mixing ratio differs also with D object, L bodies, or DL object, respectively, and L bodies is more specifically usable.

[0029] Although it will not be limited as a derivative of the amino acid which has a thiol group in the intramolecular in above-mentioned \*\*\*\* and above-mentioned this invention especially if it has a metallic corrosion prevention operation, the carboxylate object of the amino acid concerning N-acyl object or this invention of amino acid which relates, for example to this invention etc. is mentioned.

[0030] An acyl group is introduced into the hydrogen atom of the amino group which the amino acid concerning \*\*\*\* this invention described above as N-acyl object of the amino acid concerning this invention has. As shown in the following general formula [2], specifically, an acyl group is introduced into the hydroxyl group of the amino group in the above-mentioned general formula [1].

[0031]

[Formula 2]

[0032] (R1 shows an acyl group among a formula, and R is the same as the above.)

[0033] As an acyl group shown by R1 in the acyl group or general formula [2] introduced into the hydrogen atom of the amino group which the amino acid concerning this invention has The shape of a straight chain, the shape of branching, and annular are sufficient. For example, a formyl group, an acetyl group, A propionyl radical, a butyryl radical, an isobutyryl radical, a valeryl radical, an iso valeryl radical, A pivaloyl radical, a hexa noil radical, a cyclo propionyl carbonyl group, The thing of the saturation aliphatic series monocarboxylic acid origin of the carbon numbers 1-6, such as a cyclopentyl carbonyl group and a cyclohexyl carbonyl group, For example, an acryloyl radical, a PUROPIO roil radical, a methacryloyl radical, a KUROTO noil radical, The thing of the partial saturation aliphatic series monocarboxylic acid origin of the carbon numbers 3-7, such as an iso KUROTO noil radical, For example, benzoyl, a naphthoyl radical, a pen TAREN carbonyl group, an in DEREN carbonyl group, An azulene carbonyl group, a HEPUTAREN carbonyl group, an indacene carbonyl group, An anthracene carbonyl group, a phenanthrene carbonyl group, a triphenylene carbonyl



group, A pyrene carbonyl group, a naphthacene carbonyl group, a PIRIREN carbonyl group, the carbon numbers 7-23, such as a pentacene carbonyl group, — desirable — the thing of the aromatic series monocarboxylic acid origin of carbon numbers 7-12 — For example, a phenylmethyl carbonyl group, a phenylethyl carbonyl group, A phenylpropyl carbonyl group, a phenyl isopropyl carbonyl group, A phenyl butyl carbonyl group, a phenyl isobutyl carbonyl group, a phenyl pentyl carbonyl group, A phenyl isopentyl carbonyl group, a phenyl neopentyl carbonyl group, A phenyl hexyl carbonyl group, a phenyl iso hexyl carbonyl group, A phenylethyl pentyl carbonyl group, a phenylmethyl pentyl carbonyl group, A phenyl dimethyl butyl carbonyl group, a phenylethyl butyl carbonyl group, A phenyl heptyl carbonyl group, a phenylmethyl hexyl carbonyl group, A phenyl dimethyl pentyl carbonyl group, a phenyl octyl carbonyl group, A phenyl nonyl carbonyl group, a phenyl DESHIRU carbonyl group, a phenyl undecyl carbonyl group, A phenyl dodecyl carbonyl group, a phenyl tridecyl carbonyl group, A phenyl cyclo propylcarbonyl radical, a phenyl cyclopentyl carbonyl group, A phenyl cyclohexyl carbonyl group, a phenyl cyclohexyl carbonyl group, A phenyl cycloheptyl carbonyl group, a phenyl cyclo octyl carbonyl group, A phenyl cyclo nonyl carbonyl group, a phenyl cyclodecyl carbonyl group, the carbon numbers 7-20, such as a phenyl cyclo undecyl carbonyl group, a phenyl cyclo dodecyl carbonyl group, and a phenyl cyclo tridecyl carbonyl group, — the thing of the aralkyl monocarboxylic acid origin of carbon numbers 7-13 etc. is mentioned preferably. In addition, in the ring of the above-mentioned acyl group of the \*\*\*\* aromatic series monocarboxylic acid origin, or the acyl group of the aralkyl monocarboxylic acid origin, you may have low-grade alkyl groups, such as a methyl group and an ethyl group, etc. as a substituent. Also in the above-mentioned \*\*\*\* acyl group, the thing of the saturation aliphatic series monocarboxylic acid origin and the thing of the aralkyl monocarboxylic acid origin are desirable, are a thing of the saturation aliphatic series monocarboxylic acid origin more preferably, and are a thing of the straight chain-like saturation aliphatic series monocarboxylic acid origin still more preferably. Also in the acyl group of the straight chain-like saturation aliphatic series monocarboxylic acid origin, especially an acetyl group is desirable.

[0034] moreover, N-acyl object of the amino acid which has a thiol group in the intramolecular concerning this invention — a commercial item (for example, product made from Wako Pure Chem Industry) — you may use — the very thing — according to a well-known approach, it may prepare suitably and you may use.

[0035] As an N-acyl object of the amino acid concerning this invention To the hydrogen atom of the amino group which the amino acid concerning this invention has

N-ARARUKA noil object with which the acyl group of N-alkanoyl object (that whose R1 in a general formula [2] is the acyl group of the saturation aliphatic series monocarboxylic acid origin) with which the acyl group of the saturation aliphatic series monocarboxylic acid origin was introduced, and the aralkyl monocarboxylic acid origin was introduced (That whose R1 in a general formula [2] is the acyl group of the aralkyl monocarboxylic acid origin) is desirable, and is N-alkanoyl object more preferably. Still more preferably It is N-straight chain alkanoyl object (that whose R1 in a general formula [2] is the acyl group of the straight chain-like saturation aliphatic series monocarboxylic acid origin) with which the acyl group of the straight chain-like saturation aliphatic series monocarboxylic acid origin was introduced into the hydrogen atom of the amino group which the amino acid concerning this invention has. Especially N-acetyl object (that whose R1 in a general formula [2] is an acetyl group) with which the acetyl group was introduced into the hydrogen atom of the amino group which the amino acid concerning this invention has especially is desirable. As an example of N-acyl object (compound shown by the general formula [2]) of the amino acid concerning this invention For example, N-acetylcysteine, N-butyryl cysteine, N-cyclohexyl carbonyl cysteine, N-PUROPIO roil cysteine, N-KUROTO noil cysteine, N-benzoyl cysteine, N-naphthoyl cysteine, N-phenylmethyl carbonyl cysteine, N-phenyl butyl carbonyl cysteine, N-phenyl cyclohexyl carbonyl cysteine, N-acetyl homocysteine, N-butyryl homocysteine, N-cyclohexyl carbonyl homocysteine, N-PUROPIO roil homocysteine, N-KUROTO noil homocysteine, N-benzoyl homocysteine, N-naphthoyl homocysteine, N-phenylmethyl carbonyl homocysteine, N-phenyl butyl carbonyl homocysteine, N-phenyl cyclohexyl carbonyl homocysteine, etc. are mentioned, and, as for these, even the mixture of D object from which a mixing ratio differs also with D object, L bodies, or DL object, respectively, and L bodies is usable.

[0036] The carboxyl group which the amino acid concerning \*\*\*\*\* this invention described above as the carboxylate object of the amino acid concerning this invention has is esterified. As shown in the following general formula [2], specifically, an acyl group is introduced into the hydroxyl group of the carboxyl group in the above-mentioned general formula [1].

[0037]

[Formula 3]

[0038] (R2 shows hydrocarbon residue among a formula, and R is the same as the above.)

[0039] In a general formula [3], as hydrocarbon residue shown by R2, as long as it is the radical of monovalence, any of aliphatic series, aromatic series, aroma aliphatic series, or an alicycle group are sufficient, and as aliphatic series in aliphatic series and aroma aliphatic series, it may be [ being saturation ] unsaturated, or the shape of the shape of a straight chain and branching has. As a typical thing of these, the alkyl group of the shape of a straight chain, the shape of branching, annular saturation, or partial saturation, an aryl group, an aralkyl radical, an alkenyl radical, etc. are mentioned, for example. The thing of 1-4 is mentioned more preferably. as an alkyl group — usually — the thing of carbon numbers 1-10 — desirable — the thing of 1-6 — specifically For example, a methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl radical, an iso-pentyl radical, a sec-pentyl radical, a tert-pentyl radical, A neopentyl radical, n-hexyl group, an iso-hexyl group, 3-methyl pentyl radical, 2-methyl pentyl radical, 1, 2-dimethyl butyl, a sec-hexyl group, A tert-hexyl group, n-heptyl radical, an iso-heptyl radical, a sec-heptyl radical, n-octyl radical, an iso-octyl radical, a sec-octyl radical, n-nonyl radical, n-decyl group, a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, a cycloheptyl radical, a cyclo octyl radical, a cyclodecyl radical, etc. are mentioned. As an aryl group, the thing of carbon numbers 6-14 is usually mentioned, a phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 2, 3-xylyl group, 2, 4-xylyl group, 2, 5-xylyl group, 2, 6-xylyl group, 3, 5-xylyl group, a naphthyl group, an anthryl radical, etc. specifically mention, and it is \*\*\*\*. as an aralkyl radical — usually — the thing of carbon numbers 7-12 — the thing of 7-10 is mentioned preferably and, specifically, benzyl, a phenethyl radical, a phenylpropyl radical, phenyl butyl, a phenyl hexyl group, a methylbenzyl radical, a methyl phenethyl radical, ethyl benzyl, etc. are mentioned. In addition, in the ring of the above-mentioned \*\*\*\* aryl group or an aralkyl radical, you may have low-grade alkyl groups, such as a methyl group and an ethyl group, a halogen atom, a nitro group, the amino group, etc. as a substituent. As an alkenyl radical, the thing of 2-10 is usually mentioned. Specifically For example, a vinyl group, an allyl group, 1-propenyl radical, an iso-propenyl radical, 3-butenyl group, 2-butenyl group, 1-butenyl group, 1, 3-swine dienyl radical, 4-pentenyl radical, 3-pentenyl radical, 2-pentenyl radical, 1-pentenyl radical, A 1, 3-pentadienyl radical, 2, 4-pentadienyl radical, 1, and 1-dimethyl-2-propenyl radical, A 1-ethyl-2-propenyl radical, 1, and 2-dimethyl-1-propenyl radical, A 1-methyl-1-butenyl group, a 5-hexenyl radical, a 4-hexenyl radical, A 2-hexenyl radical, a 1-hexenyl radical, a 1-methyl-1-hexenyl

radical, A 2-methyl-2-hexenyl radical, the 3-methyl 1, 3-hexa dienyl radical, 1-heptanyl radical, 2-octenyl group, 3-NONENIRU radical, 4-decenyl radical, 2-cyclo pentenyl radical, 2, 4-cyclopentadienyl group, 1-cyclohexenyl group, 2-cyclohexenyl group, 3-cyclohexenyl group, 2-cycloheptenyl group, 2-cyclo NONENIRU radical, 3-cyclo decenyl radical, etc. are mentioned. Especially, an alkyl group and an aralkyl radical are desirable, are the low-grade alkyl group and benzyl of carbon numbers 1-6 more preferably, and are a low-grade alkyl group of carbon numbers 1-6 still more preferably.

[0040] the carboxylate object of the amino acid which has a thiol group in the intramolecular concerning this invention — a commercial item (for example, product made from Wako Pure Chem Industry) — you may use — the very thing — according to a well-known approach, it may prepare suitably and you may use.

[0041] As a carboxylate object of the amino acid concerning this invention To the carboxyl group which the amino acid concerning this invention has The aralkyl ester object (that whose R2 in a general formula [3] is an aralkyl radical) with which the alkyl ester object (that whose R2 in a general formula [3] is the alkyl group) and aralkyl radical into which the alkyl group was introduced were introduced is desirable. To the carboxyl group which the amino acid more preferably applied to this invention has It is the benzyl ester object (that whose R2 in a general formula [3] is benzyl) with which low-grade alkyl ester \*\*\*\* (that whose R2 in a general formula [3] is the low-grade alkyl group of carbon numbers 1-6) and benzyl into which the alkyl group of carbon numbers 1-6 was introduced were introduced. Furthermore, it is a low-grade alkyl ester object preferably. As an example of the carboxylate object (compound shown by the general formula [3]) of the amino acid concerning this invention For example, cysteine methyl ester, cysteine ethyl ester, cysteine isobutyl ester, Cysteine n-hexyl ester, cysteine cyclohexyl ester, Cysteine phenyl ester, cysteine naphthyl ester, cysteine benzyl ester, Cysteine methylbenzyl ester, cysteine vinyl ester, cysteine 3-butenyl ester, Cysteine 3-cyclohexenyl ester, homocysteine methyl ester, Homocysteine ethyl ester, homocysteine isobutyl ester, Homocysteine n-hexyl ester, homocysteine cyclohexyl ester, Homocysteine phenyl ester, homocysteine naphthyl ester, Homocysteine benzyl ester, homocysteine methylbenzyl ester, Homocysteine vinyl ester, homocysteine 3-butenyl ester, homocysteine 3-cyclohexenyl ester, etc. are mentioned, and, as for these, even the mixture of D object from which a mixing ratio differs also with D object, L bodies, or DL object, respectively, and L bodies is usable.

[0042] The amino acid which has a thiol group in the intramolecular concerning above-mentioned \*\*\*\* this invention, or its derivative may be used independently, or two or more sorts, it may combine suitably and it may be used.

[0043] Although the amount of the amino acid which has a thiol group in intramolecular, or its derivative used does not generally have \*\*\*\*\* since it changes with the class of the amino acid which has a thiol group in intramolecular, or its derivative, surface areas of the substrate processed, etc., it is 0.0001 - 10 % of the weight usually 0.0001 - 0.5 % of the weight more preferably 0.0001 to 1% of the weight.

[0044] The metal corrosion inhibitor of this invention comes to contain in the intramolecular concerning above-mentioned \*\*\*\* this invention the amino acid which has a thiol group, or its derivative. Moreover, the metal corrosion inhibitor of this invention is usually in the condition of an aqueous solution, and is prepared by making water carry out the addition dissolution of the amino acid concerning this invention concerned, or its derivative.

[0045] As an approach of dissolving the amino acid concerning this invention, or its derivative in water, the approach of adding the amino acid concerning this invention which dissolved separately, for example into water, or its derivative, the approach of adding the amino acid concerning this invention or its derivative in direct water, and dissolving and stirring, etc. are mentioned.

[0046] Thus, as for the prepared metal corrosion inhibitor of this invention, it is desirable to perform filtration processing etc. before use. Moreover, although the water used here should just be refined by distillation, ion exchange treatment, etc., the so-called ultrapure water used in this field is more desirable.

[0047] Furthermore, into the metal corrosion inhibitor concerning this invention, the reagents usually used in this field in addition to the amino acid concerning above-mentioned \*\*\*\* this invention or its derivative can be used. As such reagents, they are an organic acid, an amine, an inorganic alkali compound, a chelating agent, a surfactant, etc., for example.

[0048] That what is necessary is just what is usually used in this field as an organic acid used in this invention Although not limited especially, for example Oxalic acid, a malonic acid, a succinic acid, a glutaric acid, An adipic acid, a pimelic acid, a suberic acid, a 2-n-butyl malonic acid, a maleic acid, The dicarboxylic acid of the carbon numbers 2-8 of a fumaric acid, a citraconic acid, mesaconic acid, a phthalic acid, isophthalic acid, a terephthalic acid, etc., For example, with a carbon numbers [ of tricarballic acid benzene tricarboxylic acid, etc. ] of six or more tricarboxylic acid, For example, with a carbon numbers [ , such as tartronic acid and a malic acid, ] of three or more mono-hydroxy dicarboxylic acid, For example, with a carbon numbers [ , such as with a carbon numbers / of a tartaric acid etc. / of four or more dihydroxy dicarboxylic acid, for example a citric acid etc., ] of six or more mono-hydroxy tricarboxylic acid, for

example, hydroxy tricarboxylic acid, such ammonium salt, etc. are mentioned. Especially, dicarboxylic acid, mono-hydroxy dicarboxylic acid, mono-hydroxy tricarboxylic acid, and dihydroxy dicarboxylic acid are desirable, and dicarboxylic acid and especially mono-hydroxy tricarboxylic acid are desirable. Oxalic acid, a malonic acid, a phthalic acid, a malic acid, a citric acid, and a tartaric acid are desirable, and, more specifically, a citric acid and especially oxalic acid are desirable. Moreover, these organic acids may be used independently, or two or more sorts, it may combine suitably and they may be used. Although the amount of the organic acid used does not generally have \*\*\*\*\* since it changes with classes of organic acid, it is 0.0001 - 20 % of the weight usually 0.05 - 10 % of the weight more preferably 0.001 to 10% of the weight.

[0049] That what is necessary is just what is usually used in this field as an amine used in this invention Although not limited especially, for example Monomethylamine, ethylamine, n propylamine, N butylamine, n-pentylamine, n-hexylamine, a cyclopentyl amine, The alkylamine of the carbon numbers 1-6, such as cyclohexylamine, for example, dimethylamine, the carbon numbers 2-12, such as a methylethyl amine, diethylamine, and a dipropyl amine, — desirable — the dialkyl amine of carbon numbers 2-6 — For example, a trimethylamine, dimethyl ethylamine, methyl diethylamine, the carbon numbers 3-18, such as triethylamine and tripropylamine, — desirable — the alkylamine of carbon numbers 3-6 — For example, monoethanolamine, diethanolamine, triethanolamine, the carbon numbers 1-18, such as dimethylethanolamine and diethyl ethanolamine, — desirable — the monochrome of carbon numbers 1-6 thru/or trihydroxy alkylamine — For example, methylene diamine, ethylenediamine, propylenediamine, Isopropanal pyrene diamine, butylene diamine, methyl methylene diamine, Ethyl ethylenediamine, methyl ethylene diamine, methyl propylenediamine, ethyl propylenediamine and pentene diamine — passing — xylene diamine — To cyclo pentene diamine and cyclo, the alkylene diamine of the carbon numbers 1-6, such as xylene diamine, for example, the carbon numbers 2-12, such as dimethylene triamine and diethylenetriamine, — desirable — the dialkylenetriamine of carbon numbers 2-4 — for example, the carbon numbers 3-18, such as a trimethylene tetramine and triethylenetetramine, — desirable — the thoria RUKIREN tetramine of carbon numbers 3-6 — For example, tetramethylammonium hydroxide, tetraethylammonium hydroxide, Tetra-n-propyl ammonium hydroxide, tetra-n-butyl ammonium hydroxide, Tetra-n-pentyl ammonium hydroxide, tetra-n-hexyl ammonium hydroxide, (The tetra-alkylammonium hydroxide [4], for example, following general formula, of the carbon numbers 4-24, such as tetracyclo pentyl ammonium hydroxide and tetracyclo hexyl ammonium hydroxide)

[0050]

[Formula 4]

[0051] (— R3 shows an alkyl group among a formula, R4 and R5 show an alkylene group, and m and n show a positive integer.) — the alkylamine-alkylene oxide addition product shown is mentioned. In a general formula [4], as an alkyl group shown by R3 The thing of 1-4 is mentioned more preferably. for example, the thing of the shape of a straight chain, the shape of branching, and the annular usual carbon numbers 1-10 — desirable — the thing of 1-6 — specifically For example, a methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl radical, an iso-pentyl radical, a sec-pentyl radical, a tert-pentyl radical, A neopentyl radical, n-hexyl group, an iso-hexyl group, 3-methyl pentyl radical, 2-methyl pentyl radical, 1, 2-dimethyl butyl, a sec-hexyl group, A tert-hexyl group, n-heptyl radical, an iso-heptyl radical, a sec-heptyl radical, n-octyl radical, an iso-octyl radical, a sec-octyl radical, n-nonyl radical, n-decyl group, a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, a cycloheptyl radical, a cyclo octyl radical, a cyclodecyl radical, etc. are mentioned. Especially a cyclohexyl radical etc. is desirable especially. as the alkylene group shown by R4 and R5 — the low-grade alkylene group of the shape of a straight chain, the shape of branching, and the annular carbon numbers 1-6 — desirable — for example, a methylene group, ethylene, a propylene radical, a butylene radical, a methyl methylene group, ethyl ethylene, a methyl ethylene radical, a methyl propylene radical, an ethyl propylene radical, and a pentene radical — it passes, a xylene radical etc. is mentioned to a xylene radical, a cyclo pentene radical and cyclo, and a methylene group, especially ethylene, etc. are desirable especially moreover, m and n — a positive integer — being shown — usually — 1-10 — it is 1-5 preferably. As an alkylamine-alkylene oxide addition product shown by the above-mentioned \*\*\*\* general formula [4] Specifically For example, methyl AMINJI (polyoxymethylene), methyl AMINJI (polyoxyethylene), Methyl AMINJI (polyoxy ethyl propylene), methyl AMINJI (polyoxy cyclo hexylene), Monomethylamine (polyoxymethylene) (polyoxyethylene), monomethylamine (polyoxymethylene) (polyoxy ethyl propylene), Monomethylamine (polyoxymethylene) (polyoxy cyclo hexylene), Monomethylamine (polyoxyethylene) (polyoxy ethyl propylene), Monomethylamine (polyoxyethylene)

(polyoxy cyclo hexylene), Monomethylamine (polyoxy ethyl propylene) (polyoxy cyclo hexylene), Ethyl AMINJI (polyoxymethylene), ethyl AMINJI (polyoxyethylene), Ethyl AMINJI (polyoxy ethyl propylene), ethyl AMINJI (polyoxy cyclo hexylene), Ethylamine (polyoxymethylene) (polyoxyethylene), ethylamine (polyoxymethylene) (polyoxy ethyl propylene), Ethylamine (polyoxymethylene) (polyoxy cyclo hexylene), Ethylamine (polyoxyethylene) (polyoxy ethyl propylene), Ethylamine (polyoxyethylene) (polyoxy cyclo hexylene), Ethylamine (polyoxy ethyl propylene) (polyoxy cyclo hexylene), Propylure MINJI (polyoxymethylene), propylure MINJI (polyoxyethylene), Propylure MINJI (polyoxy ethyl propylene), propylure MINJI (polyoxy cyclo hexylene), Propylamine (polyoxymethylene) (polyoxyethylene), propylamine (polyoxymethylene) (polyoxy ethyl propylene), Propylamine (polyoxymethylene) (polyoxy cyclo hexylene), Propylamine (polyoxyethylene) (polyoxy ethyl propylene), Propylamine (polyoxyethylene) (polyoxy cyclo hexylene), Alkyl AMINJI, such as propylamine (polyoxy ethyl propylene) (polyoxy cyclo hexylene) (polyoxyalkylene), For example, cyclohexyl AMINJI (polyoxymethylene), cyclohexyl AMINJI (polyoxyethylene), Cyclohexyl AMINJI (polyoxypropylene), cyclohexyl AMINJI (polyoxy butylene), Cyclohexyl AMINJI (polyoxy methyl methylene), cyclohexyl AMINJI (polyoxy ethyl ethylene), Cyclohexyl AMINJI (polyoxy ethyl propylene), cyclohexyl AMINJI (polyoxy pentene), Cyclohexyl AMINJI (it is a xylene to polyoxy), cyclohexyl AMINJI (polyoxy cyclo hexylene), Cyclohexylamine (polyoxymethylene) (polyoxyethylene), Cyclohexylamine (polyoxymethylene) (polyoxy ethyl propylene), Cyclohexylamine (polyoxymethylene) (polyoxy cyclo hexylene), Cyclohexylamine (polyoxyethylene) (polyoxy ethyl propylene), Cyclohexylamine (polyoxyethylene) (polyoxy cyclo hexylene), Cyclohexylamine (polyoxy ethyl propylene) (polyoxy cyclo hexylene), Cyclodecyl AMINJI (polyoxymethylene), cyclodecyl AMINJI (polyoxyethylene), Cyclodecyl AMINJI (polyoxy ethyl propylene), cyclodecyl AMINJI (polyoxy cyclo hexylene), A cyclodecyl amine (polyoxymethylene) (polyoxyethylene), A cyclodecyl amine (polyoxymethylene) (polyoxy ethyl propylene), A cyclodecyl amine (polyoxymethylene) (polyoxy cyclo hexylene), A cyclodecyl amine (polyoxyethylene) (polyoxy ethyl propylene), Cycloalkyl AMINJI (polyoxyalkylene), such as a cyclodecyl amine (polyoxyethylene) (polyoxy cyclo hexylene) and a cyclodecyl amine (polyoxy ethyl propylene) (polyoxy cyclo hexylene), etc. is mentioned.

[0052] Also in the above-mentioned \*\*\*\* amine, alkylene diamine, dialkylenetriamine, a thoria RUKIREN tetramine, an alkylamine-alkylene oxide addition product, and tetra-alkylammonium hydroxide are desirable, and alkylene diamine and especially



cycloalkyl AMINJI (polyoxyalkylene) are desirable especially. Ethylenediamine, diethylenetriamine, triethylenetetramine, cyclohexyl AMINJI (polyoxyethylene), cyclohexylamine (polyoxyethylene) (polyoxymethylene), and tetramethylammonium hydroxide are desirable, and, specifically, ethylenediamine and especially cyclohexyl AMINJI (polyoxyethylene) are desirable especially. Moreover, these amines may be used independently, or two or more sorts, it may combine suitably and they may be used. Although the amount of the amine used does not generally have \*\*\*\*\* since it changes with classes of amine, it is 0.0001 - 20 % of the weight usually 0.05 - 10 % of the weight more preferably 0.001 to 10% of the weight.

[0053] That what is necessary is just what is usually used in this field as an inorganic alkali compound used in this invention, although not limited especially, inorganic alkali, such as nitrogen content inorganic alkali compounds, for example, a potassium hydroxide, such as a hydroxy amine, a hydrazine, ammonia, and these salts (for example, a hydrochloride, a sulfate, etc.), and a sodium hydroxide, etc. is mentioned, for example. Especially, a nitrogen content inorganic alkali compound is desirable, and the nitrogen content inorganic alkali compound which does not contain a metal especially is desirable. A hydroxylamine, a hydrazine, and ammonia are specifically desirable, and ammonia is desirable especially. Moreover, these inorganic alkali compound may be used independently, or two or more sorts, it may combine suitably and it may be used. Although the amount of the inorganic alkali compound used does not generally have \*\*\*\*\* since it changes with classes of inorganic alkali compound, it is 0.0001 - 20 % of the weight usually 0.05 - 10 % of the weight more preferably 0.001 to 10% of the weight.

[0054] It is not limited especially that what is necessary is just what is usually used in this field as a chelating agent used in this invention. By adding a chelating agent, metallic oxides, such as copper oxide distributed in liquid, can be solubilized, and re-adsorption can be suppressed, and impurities, such as Fe and aluminum, can also be removed from a substrate front face. As such a chelating agent, for example EDTA (ethylenediaminetetraacetic acid), EDDA (ethylenediamine 2 acetic acid), EDTA-OH (hydroxy ethylenediamine triacetic acid), GEDTA (glycol ether diamine tetraacetic acid), DTPA (diethylenetriamine pentaacetic acid), IDA (iminodiacetate), methyl-EDTA (diaminopropane tetraacetic acid), NTA (nitrilotriacetic acid), TTHA (triethylenetetramine 6 acetic acid), Straight chain mold amino polycarboxylic acid, such as such ammonium salt and complex salt of these and an amine For example, CyDTA (trans-cyclohexyl diamino tetraacetic acid), Amino polycarboxylic acid, such as annular amino polycarboxylic acid, such as ammonium salt of this, and complex salt of

this and an amine For example, NTPO (nitrilotrismethylene phosphonic acid), HEDPO (hydroxy ECHIRIDENJI (methylene phosphonic acid)), Pori phosphonic acid, such as such ammonium salt and complex salt of these and an amine For example, EDDPO (ethylene JIAMINJI (methylene phosphonic acid)), EDTPO (ethylenediamine tetrapod (methylene phosphonic acid)), PDTPO (diaminopropane tetrapod (methylene phosphonic acid)), Phosphonic acid, such as amino poly phosphonic acid, such as DETPPO (diethylenetriamine PENTA (methylene phosphonic acid)), TTHPO(s) (triethylenetetramine hexa (methylene phosphonic acid)), such ammonium salt, and complex salt of these and an amine, is mentioned. Especially, EDTA, CyDTA, HEDPO, EDTPO, DETPPO(s), such ammonium salt, and especially the complex salt of these and an amine are desirable. In addition, in the above, the thing same as an amine which forms complex salt as the amine described previously is mentioned. Moreover, these chelating agents may be used independently, or two or more sorts, it may combine suitably and they may be used. Although the amount of the chelating agent used does not generally have \*\*\*\*\* since it changes with classes of chelating agent, it is 0.0001 - 10 % of the weight usually 0.0001 - 0.5 % of the weight more preferably 0.0001 to 1% of the weight.

[0055] It is not limited especially that what is necessary is just what is usually used in this field as a surfactant used in this invention. By adding a surfactant, the wettability of an aqueous solution to a substrate front face can be improved. The Nonion system surfactant which has a polyoxyalkylene group, for example in a molecule as such a surfactant, For example, the anion system surfactant which has the radical chosen from a sulfonic group, a carboxyl group, a phosphonic acid radical, a sulfo KISHIRU radical, and a phosphono KISHIRU radical into a molecule, For example, quaternary ammonium, such as alkylamine, for example, alkyl trimethylammonium, and alkyl dimethylbenzyl ammonium, For example, cation system surfactants, such as alkyl pyridinium and these salts (for example, a hydrochloride, a sulfate, etc.), For example, although amphoteric surface active agents, such as an alkyl betaine derivative, an imidazolinium betaine derivative, a sulfobetaine derivative, an amino carboxylic-acid derivative, an imidazoline derivative, and an amine oxide derivative, etc. are mentioned, it is not limited to these. As an Nonion system surfactant which has a polyoxyalkylene group in a molecule Polyoxyalkylene alkyl ether, the polyoxyalkylene poly alkyl aryl ether, etc. are mentioned. For example, more specifically For example, the Nonion system surfactant which has a polyoxyethylene radical in molecules, such as polyoxyethylene alkyl ether and polyoxyethylene alkyl phenyl ether, For example, the Nonion system surfactant which has a polyoxypropylene radical in molecules, such as

polyoxypropylene alkyl ether and the polyoxypropylene alkylphenyl ether, For example, the Nonion system surfactant which has a polyoxyethylene radical and a polyoxypropylene radical is mentioned into molecules, such as polyoxyethylene polyoxypropylene alkyl ether and the polyoxyethylene polyoxypropylene alkylphenyl ether. As an anion system surfactant which has the radical chosen from a sulfonic group, a carboxyl group, a phosphonic acid radical, a sulfo KISHIRU radical, and a phosphono KISHIRU radical into a molecule For example, an alkyl sulfonic acid, alkylbenzene sulfonic acid, an alkyl naphthalene sulfonic acid, These salts (for example, alkali-metal salts, for example, ammonium salt etc., such as sodium and a potassium) The anion system surfactant which has a sulfonic group in a molecule, like ammonium salt is desirable especially, For example, an alkyl carboxylic acid, an alkylbenzene carboxylic acid, an alkyl naphthalene carboxylic acid, These salts (for example, alkali-metal salts, for example, ammonium salt etc., such as sodium and a potassium) The anion system surfactant which has a carboxyl group in a molecule, like ammonium salt is desirable especially, For example, alkyl phosphonic acid, alkylbenzene phosphonic acid, alkyl naphthalene phosphonic acid, These salts (for example, alkali-metal salts, for example, ammonium salt etc., such as sodium and a potassium) The anion system surfactant which has a phosphonic acid radical in a molecule, like ammonium salt is desirable especially, For example, alkyl-sulfuric-acid ester, an alkylbenzene sulfate, polyoxyethylene alkyl-sulfuric-acid ester, A polyoxyethylene alkylbenzene sulfate, a polyoxyethylene alkyl naphthalene sulfate, The anion system surfactant which has a sulfo KISHIRU radical is mentioned into molecules, such as these salts (for example, alkali-metal salts, for example, ammonium salt etc., such as sodium and a potassium, have desirable ammonium salt especially). Especially, the Nonion system surfactant and an anion system surfactant are desirable. Moreover, especially as an Nonion system surfactant, polyoxyalkylene alkyl ether is desirable, and what has a sulfonic group in a molecule, and especially the thing that has a sulfo KISHIRU radical in a molecule are desirable as an anion system surfactant. Especially the anion system surface active agent that has a sulfo KISHIRU radical in molecules, such as an anion system surface active agent which has a carboxyl group in molecules, such as the Nonion system surface active agent which has a polyoxyethylene radical and a polyoxypropylene radical in molecules, such as the Nonion system surface active agent which more specifically has a polyoxyethylene radical in molecules, such as polyoxyethylene alkyl ether, and polyoxyethylene polyoxypropylene alkyl ether, and alkylbenzene sulfonic acid, and polyoxyethylene alkyl-sulfuric-acid ester, is desirable. Moreover, these surfactants may be used independently, or two or more sorts, it may combine suitably and they may be

used. Since the amount of the surfactant used changes with classes of surfactant, it does not generally have \*\*\*\*\*, but that the Nonion system surfactant should just be more than critical micelle concentration, if thinner than it, the rate of etching will become quick and effectiveness will fade. Moreover, surfactants other than a nonionic surfactant should just be the amounts in which the surface tension of a substrate finishing agent may be reduced. Although there is no \*\*\*\*\* generally as the concrete amount used since it changes with classes of surfactant, it is 0.0001 - 1 % of the weight usually 0.0001 - 0.05 % of the weight more preferably 0.0001 to 0.1% of the weight.

[0056] The metal corrosion inhibitor of this invention has the desirable thing which comes to contain the amino acid concerning above-mentioned \*\*\*\* this invention or its derivative, and at least 1 of the above-mentioned \*\*\*\* organic acid, an amine, an inorganic alkali compound, a chelating agent, and surfactants, and especially its thing that comes to contain the amino acid concerning above-mentioned \*\*\*\* this invention or its derivative, and a chelating agent or/and a surfactant is still more desirable.

[0057] By sticking to the metal corrosion inhibitor of this invention in the surface of metal which the amino acid which has a thiol group in the intramolecular concerning this invention contained there, or its derivative has, and forming a protective coat in the front face concerned If the property in which oxidation and corrosion of the metal which protects a surface of metal and wins popularity out of a water solution or air can be controlled is used and the substrate front face which has the metallic-coating section on a front face is processed, using the metal corrosion inhibitor of this invention Oxidation and corrosion of the metal on the front face of a substrate concerned can be prevented, and the metal impurity on the front face of a substrate can be removed further effectively.

[0058] It comes to contain the processing agent of this invention by the \*\*\*\* density range which mentioned above reagents usually used in this field, such as the amino acid which has a thiol group in the intramolecular concerning the metal corrosion inhibitor of above-mentioned \*\*\*\* this invention, i.e., this invention, or its derivative, \*\*\*\* mentioned above, for example, an organic acid, an amine, an inorganic alkali compound, a chelating agent, and a surfactant, when requiring. In addition, if at least one of the reagents used \*\*\*\* usual at this rate [ above-mentioned ] in the fields is made to contain in the processing agent of this invention, metal impurities (for example, metallic oxides, such as oxidation copper and ferrous oxide etc.), particle, etc. can be more effectively removed to preventing oxidation and corrosion of the metal on the front face of a substrate, and coincidence. Especially the thing that comes to contain the amino acid applied to above-mentioned \*\*\*\* this invention especially or its derivative, and a

chelating agent or/and a surfactant is desirable. The above-mentioned example of \*\*\*\* reagents, a desirable mode, etc. are as having stated previously.

[0059] The processing agent of this invention is usually in the condition of an aqueous solution, and is prepared by making water carry out the addition dissolution of the amino acid concerning this invention concerned, or its derivative by the same preparation approach as the metal corrosion inhibitor of \*\*\*\* this invention mentioned above.

[0060] Thus, as for the processing agent of prepared this invention, it is desirable to perform filtration processing etc. before use.

[0061] The art (the metal corrosion prevention approach) of this invention contacts the processing agent (metal corrosion inhibitor) of above-mentioned \*\*\*\* this invention, and the metal on the front face of a substrate which has the metallic-coating section on a front face, and should just process the substrate front face concerned by the processing agent (the metal corrosion prevention approach) of this invention.

[0062] the very thing usually performed in this field as an approach of processing the substrate front face which has the metallic-coating section on a front face by the processing agent (the metal corrosion prevention approach) of this invention — specifically, approaches, such as DIP processing only immersed into a processing agent (metal corrosion inhibitor) in a substrate and sheet processing which sprinkles a processing agent over a substrate in the shape of a shower, are mentioned that what is necessary is just a well-known approach.

[0063] In this invention, as described above as "processing", it says contacting the processing agent of this invention, and the metal on the front face of a substrate. Although pretreatment before giving preservation processing, for example, washing processing etc., washing processing, etc. are more specifically mentioned, it is not limited to these.

[0064] That is, the metal corrosion inhibitor of this invention can be used also as processing agents, such as a preservative for substrates which has the metallic-coating section on a front face, a pretreatment agent for substrates which has the metallic-coating section on a front face, or a cleaning agent for substrates which has the metallic-coating section on a front face.

[0065] For example, if the processing agent of this invention is used for a front face as a preservative for substrates which has the metallic-coating section, the oxidation and corrosion in which the metal concerned receives during substrate preservation can be prevented, and the metal impurity on the front face of a substrate can also be further removed from various ambient atmospheres, such as a water solution and air, effectively.

After performing the approaches of saving performing the approach of saving while \*\*\*\* DIP processing described above, for example was performed as a store method of the substrate of this invention and the substrate had been immersed into the processing agent (preservative) of this invention, the above-mentioned \*\*\*\* sheet processing, etc., and sprinkling the processing agent (preservative) of this invention over a substrate, or these processings, the method of drying and saving a substrate etc. is mentioned.

[0066] Moreover, if it uses as a pretreatment agent for the substrates concerned and the metal on the front face of a substrate is processed before \*(ing) the substrate which has the metallic-coating section for the processing agent of this invention on a front face at a washing process etc., for example The oxidation and corrosion which a metal receives into the process of degree process can be prevented, and easy actuation of washing by ultrapure water etc. can remove effectively the metal impurity on the front face of a substrate from various ambient atmospheres, such as air while water solutions and degree processes, such as a cleaning agent used at degree process, \*\*, further. After performing the approach immersed in a substrate into the processing agent (pretreatment agent) of this invention by \*\*\*\* DIP processing described above, for example as the pretreatment approach of the substrate of this invention, the approaches of sprinkling the processing agent (pretreatment agent) of this invention over a substrate by the above-mentioned \*\*\*\* sheet processing, or these processings, the approach of drying a substrate etc. is mentioned.

[0067] thus, the very thing to which the obtained substrate is usually performed in this field — it can \* to the washing approach using a well-known finishing agent (cleaning agent). As a finishing agent (cleaning agent) used in the above Although all the things used in this field can be used and it is not limited especially For example, JP,5-263275,A, JP,6-112646,A, JP,6-287774,A, JP,7-54169,A, JP,7-79061,A, JP,7-166381,A, JP,7-292483,A, JP,2000-8185,A, The finishing agent (cleaning agent) indicated by JP,10-251867,A, JP,7-267933,A, JP,11-50275,A, etc., the cleaning agent of this invention mentioned later, etc. are mentioned.

[0068] Furthermore, if the substrate front face which uses the processing agent of this invention for a front face as a cleaning agent for substrates which has the metallic-coating section, for example, and has the metallic-coating section on a front face is processed, the corrosion and oxidation of the metal on the front face of a substrate can be prevented, and the metal impurity of the front face concerned can be removed effectively.

[0069] The amino acid which has a thiol group in the intramolecular concerning this invention as the processing agent of this invention was mentioned above, or its

derivative, The amino acid which whose thing which comes to contain at least one of \*\*\*\* and the organic acid which were mentioned above, an amine, an inorganic alkali compound, a chelating agent, and surfactants is desirable, and requires it for this invention, or its derivative, Although the thing which comes to contain a chelating agent or/and a surfactant is more desirable, in case the processing agent of this invention is used as a cleaning agent, especially considering as such a presentation is desirable. In addition, the example of the above-mentioned \*\*\*\* organic acid, an amine, an inorganic alkali compound, a chelating agent, and a surfactant, a desirable mode, etc. are as having stated previously.

[0070] The cleaning agent of this invention is usually in the condition of an aqueous solution, and is prepared by making water carry out the addition dissolution of the amino acid concerning this invention concerned, or its this, at least 1 [ or ] of an organic acid, an amine, an inorganic alkali compound, a chelating agent, and surfactants and derivative. As an approach of dissolving the amino acid concerning this invention, or its derivative in water For example, the amino acid concerning this invention which dissolved separately into water or its derivative (or with this) The approach of adding at least one of the organic acid which dissolved separately, an amine, an inorganic alkali compound, a chelating agent, and surfactants, the amino acid concerning this invention, or its derivative (or with this) the approach of adding at least one of an organic acid, an amine, an inorganic alkali compound, a chelating agent, and surfactants in direct water, and dissolving and stirring — or The approach of stirring and mixing at least one of the organic acid and amine which added in water separately and dissolved with the amino acid concerning this invention which added and dissolved into water, or its derivative, an inorganic alkali compound, a chelating agent, and surfactants etc. is mentioned.

[0071] Thus, as for the prepared cleaning agent of this invention, it is desirable to perform filtration processing etc. before use. Moreover, although the water used here should just be refined by distillation, ion exchange treatment, etc., the so-called ultrapure water used in this field is more desirable.

[0072] What is necessary is just to process the washing approach of this invention with the cleaning agent of \*\*\*\* this invention which described above the substrate front face which has the metallic-coating section on a front face.

[0073] the very thing usually performed in this field as an approach of processing the substrate front face which has the metallic-coating section on a front face with the cleaning agent of this invention — approaches mentioned above, such as \*\*\*\* DIP processing and sheet processing, are mentioned that what is necessary is just the well-known washing approach.

[0074] Furthermore, in this invention, metal impurities (oxidation equivalent metallic oxide etc.) can be more effectively removed by using physical washing together at the time of washing. Giving the substrate front face which has the metallic-coating section on a front face to a physical washing process under existence of the cleaning agent of this invention as the concrete approach of concomitant use etc. is mentioned.

[0075] In the above-mentioned approach, the approach of giving to a physical washing process as a condition in which the cleaning agent of this invention was made to specifically exist by the above-mentioned \*\*\*\* DIP processing, sheet processing, etc. as an approach in which the cleaning agent of this invention is made to exist etc. is mentioned. Moreover, brush scrub washing which washes a substrate front face, for example, using the brush made from polyvinyl alcohol of high-speed rotation etc. as physical washing (process), megasonic washing using a RF, etc. are mentioned.

[0076] As more concrete technique in the case of using physical washing together For example, the method of performing physical washing, after considering as the condition of having taken out the substrate out of the penetrant remover concerned after being immersed into the cleaning agent of this invention, and having made the cleaning agent concerned existing in a substrate front face, How to perform physical washing after considering as the condition of having sprinkled the cleaning agent of this invention over the approach and substrate front face which perform physical washing while the substrate had been made immersed into the cleaning agent of this invention, and having made the cleaning agent concerned existing in a substrate front face, Or the method of performing physical washing etc. is mentioned, sprinkling the cleaning agent of this invention over a substrate front face.

[0077] Especially the acidity or alkalinity of the metal corrosion inhibitor of above-mentioned \*\*\*\* this invention and processing agents (a preservative, a pretreatment agent, cleaning agent, etc.) is not limited, but is suitably chosen from pH range usually used in this field by a class, the purpose, etc. of using the substrate used. more — concrete — the acescence thru/or alkalinity — desirable — usually — pH 2-13 — desirable — pH 3-12 — it is pH 4-10 more preferably. By considering as such pH range, since electric repulsion with a substrate front face and particle becomes large, the removal effectiveness of particle and metal impurities (for example, metallic oxides, such as copper oxide etc.) improves, and a possibility of etching SiO<sub>2</sub> which is an interlayer insulation film further decreases more.

[0078] The metal corrosion inhibitor and the processing agents of this invention (a preservative, a pretreatment agent, cleaning agent, etc.) can be used for the substrate which has the metallic-coating section on a front face. As such a substrate, the glass



substrate used, for example for printed circuit boards, such as a semi-conductor substrate and polyimide resin, LCD, etc. is mentioned, and it is useful to especially a semi-conductor substrate. Moreover, copper, chromium, silver, gold, etc. are mentioned and it is [ that what is necessary is just sulfur and the metal which reacts as a metal covered by the substrate front face concerned ] useful in especially metal copper. Especially, it is useful to especially the semi-conductor substrate that has the copper covering section on a front face (copper wiring was given).

[0079] Although an example and the example of a comparison are given to below, this invention is not limited at all by these.

[0080] Moreover, the amount of adsorption (residual Cu concentration) of Cu (copper atom) which the metal Cu deposition wafer and Cu contamination wafer which were used in this example and the example of a comparison use what was prepared by the following approaches, respectively, and is carrying out adsorption survival on the thickness of Cu of a metal Cu deposition wafer front face and Cu contamination wafer front face was measured by the following approaches, respectively.

[0081] [Metal Cu deposition wafer] The thing which made Metal Cu deposit on the front face of a 4 inch silicon wafer by the spatter was used as the copper deposition wafer. In addition, the thickness of the copper of the metal Cu deposition wafer front face concerned checked that it was 1000nm by the approach shown below.

[0082] [Cu contamination wafer] — for [ slurry water-solution / which added Cu ion so that the 4 inch silicon wafer which set the front face to SiO<sub>2</sub> by the oxidizing / thermally / method might be set to 1 ppm / (0.1% hydrogen peroxide solution of 1% silica content) ] 1L1 minute — being immersed — ultrapure water — for 10 minutes — a stream — after washing, what carried out spin desiccation was used as Cu contamination wafer. In addition, to the Cu contamination wafer concerned, it checked that Cu (copper atom) was carrying out  $3 \times 10^{14}$  atom / cm<sup>2</sup> adsorption survival by the approach shown below.

[0083] [Metal Cu thickness measurement method] The wafer was divided into one half, the cross section was observed with the electron microscope, and metal Cu thickness was measured.

[0084] [Cu density measurement method] On the wafer front face, after carrying out dissolution recovery of the Cu which carried out adsorption survival in a fluoric acid-nitric-acid water solution, Cu concentration in this recovery liquid was measured with the atomic absorption method (graphite furnace atomic-absorption-analysis equipment). Based on the obtained measured value, the amount of adsorption (residual Cu concentration) of Cu (copper atom) was calculated.

[0085] In addition, in this example and the example of a comparison, all especially of % which expresses concentration as long as there is no notice, and ppm and ppb show a weight ratio. Moreover, all the water to be used was ultrapure water, and it was used after checking that copper was 0.01 or less ppb.

#### **EXAMPLE**

[Example] The metal Cu deposition wafer produced by the above-mentioned approach was immersed in each metal corrosion inhibitor (preservative) 1L given in one to example 14 table 1 under the room temperature for 5 hours. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Thus, in order to observe the color tone of Cu film front face on the front face of a wafer visually in order to check the existence of oxidation of Metal Cu, and to check the existence of the corrosion of Metal Cu about the processed metal Cu deposition wafer, the thickness of the metal Cu on the front face of a wafer was measured. A result is shown in Table 1.

[0087]

[Table 1]

[0088] Except having used the various solutions of a publication for one to example of comparison 6 table 2, after processing a metal Cu deposition wafer by the same approach as examples 1-14, the color tone of Cu film front face on the front face of a wafer was observed visually, and the thickness of the metal Cu on the front face of a wafer was measured. A result is shown in Table 2. In addition, - in Table 2 shows measurement impossible.

[0089]

[Table 2]

[0090] When a metal Cu deposition wafer is saved in the metal corrosion inhibitor (preservative) (examples 1-14) of this invention so that clearly from Table 1 and 2, it is changeless to the color tone of Cu film front face on the front face of a wafer, and Metal Cu does not oxidize, and there is almost no change in Cu thickness, and it turns out that Metal Cu is not being corroded. On the other hand, when a metal Cu deposition wafer is saved in the solution of the examples 1 and 5 of a comparison, Metal Cu is corroded remarkably, and the gloss of Cu film front face on the front face of a wafer disappears, and it turns out that Metal Cu has oxidized. Moreover, although it is changeless to the color tone of Cu film front face on the front face of a wafer and Metal Cu has not oxidized when saved in the solution of the examples 4 and 6 of a comparison, Cu thickness decreases and it turns out that Metal Cu is being corroded (dissolution). Furthermore, it turns out that Metal Cu is being altogether corroded for setting for the example 2 of a comparison, and Metal Cu being oxidized and corroded (dissolution) especially in the example 3 of a comparison (dissolution). That is, the metal corrosion inhibitor of this invention can prevent metal oxidation and corrosion, if the substrate which has the metallic-coating section is saved on a front face in the processing agent (preservative) which comes to contain the metal inhibitor of this invention, oxidation and corrosion of the metal concerned can be prevented to coincidence, and it turns out that the substrate which has the metallic-coating section can be saved good in a solution on a front face.

[0091] The metal Cu deposition wafer produced by the above-mentioned approach was immersed in each metal corrosion inhibitor (preservative) 1L given in 15 to example 17 table 3 for 1 minute under the room temperature. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Subsequently, the wafer was left in air for 10 hours. Thus, in order to check the existence of oxidation of Metal Cu about the processed metal Cu deposition wafer,

the color tone of Cu film front face on the front face of a wafer was observed visually. A result is shown in Table 3.

[0092] Except having used the various solutions of a publication for seven to example of comparison 10 table 3, after processing a metal Cu deposition wafer by the same approach as examples 15-17, the color tone of Cu film front face on the front face of a wafer was observed visually. A result is combined with examples 15-17, and is shown in Table 3.

[0093]

[Table 3]

[0094] When the wafer concerned is saved in air after processing a metal Cu deposition wafer with the metal corrosion inhibitor (preservative) (examples 15-17) of this invention so that clearly from Table 3, it is changeless to the color tone of Cu film front face on the front face of a wafer, and it turns out that Metal Cu has not oxidized. On the other hand, when a metal Cu deposition wafer is processed with the solution of the examples 7-10 of a comparison, the gloss of Cu film front face on the front face of a wafer disappears, and it turns out that Metal Cu has oxidized. That is, it turns out that the substrate which can prevent oxidation of the metal on the front face of a substrate concerned, and has the metallic-coating section on a front face by the processing agent (preservative) which comes to contain the metal inhibitor of this invention if this is saved after processing the substrate which has the metallic-coating section on a front face can be saved good in air.

[0095] 18 to example 20 table 4 was sprinkled having metal covered [ of the publication / each / 500ml ] it over the metal Cu deposition wafer front face produced by the

above-mentioned approach for 1 minute (preservative). Then, with ultrapure water, the rinse of the wafer was carried out for 10 minutes, and it carried out spin desiccation. Subsequently, the wafer was left in air for 10 hours. Thus, in order to check the existence of oxidation of Metal Cu about the processed metal Cu deposition wafer, the color tone of Cu film front face on the front face of a wafer was observed visually. A result is shown in Table 4.

[0096] Except having used the various solutions of a publication for 11 to example of comparison 14 table 4, after processing a metal Cu deposition wafer by the same approach as examples 18-20, the color tone of Cu film front face on the front face of a wafer was observed visually. A result is combined with examples 18-20, and is shown in Table 4.

[0097]

[Table 4]

[0098] When the wafer concerned is saved in air after processing a metal Cu deposition wafer with the metal corrosion inhibitor (preservative) (examples 18-20) of this invention so that clearly from Table 4, it is changeless to the color tone of Cu film front face on the front face of a wafer, and it turns out that Metal Cu has not oxidized. On the other hand, when a metal Cu deposition wafer is processed with the solution of the examples 15-17 of a comparison, the gloss of Cu film front face on the front face of a wafer disappears, and it turns out that Metal Cu has oxidized. By namely, the processing agent (preservative) which comes to contain the metal inhibitor of this invention not only by the \*\*\*\*\* DIP processing performed in the examples 15-17 but by the

so-called sheet processing which was performed in the examples 18-20 If this is saved after processing the substrate which has the metallic-coating section on a front face, oxidation of the metal on the front face of a substrate concerned can be prevented, and it turns out that the substrate which has the metallic-coating section can be saved good in air on a front face.

[0099] Cu contamination wafer and the metal Cu deposition wafer which were produced by the above-mentioned approach were immersed in each metal corrosion inhibitor (pretreatment agent) 1L given in 21 to example 34 table 5 under the room temperature for 1 hour. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Subsequently, the wafer concerned was immersed in each penetrant remover 1L given in Table 5 for 10 minutes under the room temperature. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Thus, about processed Cu contamination wafer, in order to measure the residual Cu concentration which is carrying out adsorption survival on a wafer front face in order to evaluate metal impurity removal capacity, and to check the existence of oxidation of Metal Cu about a metal Cu deposition wafer, the color tone of Cu film front face on the front face of a wafer was observed visually, and further, in order to check the existence of the corrosion of Metal Cu, the thickness of the metal Cu on the front face of a wafer measured. A result is shown in Table 5. In addition, - in Table 5 shows measurement impossible.

[0100] Except having used the various solutions and each cleaning agent of a publication for 15 to example of comparison 25 table 6 After processing Cu contamination wafer and a metal Cu deposition wafer by the same approach as examples 21-34, about Cu contamination wafer The residual Cu concentration which is carrying out adsorption survival was measured on the wafer front face, and about the metal Cu deposition wafer, the color tone of Cu film front face on the front face of a wafer was observed visually, and the thickness of the metal Cu on the front face of a wafer was measured further. A result is shown in Table 6. In addition, in the examples 15-18 of a comparison, processing with metal corrosion inhibitor (pretreatment agent) was not performed, but the thing which the wafer was taken [ thing ] out to it, and the rinse was carried out [ thing ] to it for 10 minutes with ultrapure water, and made it carry out spin desiccation after the wafer concerned was immersed in each penetrant remover 1L given in Table 6 for 10 minutes under a room temperature was measured and observed.

[0101]

[Table 5]

[0102]

[Table 6]



[0103] When it pretreats using the metal corrosion inhibitor (pretreatment agent) of examples 21, 22, and 27 so that clearly from the result of Table 5 and 6, it turns out that the residual Cu concentration of Cu contamination wafer front face can be controlled for 1010 or less \*\*\*\*\*, and corrosion can be prevented in the oxidation list of Metal Cu. On the other hand, although residual Cu concentration can be controlled to the same extent, oxidation and corrosion of Metal Cu are produced or the oxidation corrosion of (the examples 19 and 23 of a comparison) and Metal Cu is suppressed when it pretreats using conventional metal corrosion inhibitor (finishing agent), residual Cu concentration is high and what (examples 20, 24, and 25 of a comparison) copper oxide cannot be effectively removed for is understood. The examples 21 and 22 of a comparison are understood that Cu film on the front face of a substrate is being corroded remarkably to the ability to remove copper oxide effectively and prevent corrosion in the oxidation list of Metal Cu in examples 23 and 30, similarly. Moreover, it also turns out that it compares when not performing this, and the oxidation and corrosion of Metal Cu at the time of washing can be controlled, and copper oxide can also be further removed from the result of examples 26, 28, 32, and 34 and the examples

15-18 of a comparison effectively if it pretreats using the metal corrosion inhibitor (pretreatment agent) of this invention. If the metal corrosion inhibitor (pretreatment agent) of this invention is used and the substrate concerned is pretreated before giving the substrate which has the metallic-coating section on a front face to a washing process so that clearly from the above thing, it can prevent that a metal receives oxidation and corrosion in a washing process, and it turns out further that a metallic oxide can also be removed effectively.

[0104] Cu contamination wafer produced by the above-mentioned approach was immersed in each cleaning agent (metal corrosion inhibitor) 1L given in 35 to example 44 table 7 for 10 minutes under the room temperature. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Moreover, the metal Cu deposition wafer produced by the above-mentioned approach was immersed in each cleaning agent (metal corrosion inhibitor) 1L given in Table 7 under the room temperature for 5 hours. Then, a wafer is taken out, with ultrapure water, the rinse was carried out for 10 minutes and spin desiccation was carried out. Thus, about processed Cu contamination wafer, in order to measure the residual Cu concentration which is carrying out adsorption survival on a wafer front face in order to evaluate metal impurity removal capacity, and to check the existence of oxidation of Metal Cu about a metal Cu deposition wafer, the color tone of Cu film front face on the front face of a wafer was observed visually, and further, in order to check the existence of the corrosion of Metal Cu, the thickness of the metal Cu on the front face of a wafer measured. A result is shown in Table 7.

[0105] Except having used each cleaning agent of a publication for 26 to example of comparison 37 table 8, after processing Cu contamination wafer and a metal Cu deposition wafer by the same approach as examples 35-44, the residual Cu concentration which is carrying out adsorption survival was measured on the wafer front face, and about the metal Cu deposition wafer, the color tone of Cu film front face on the front face of a wafer was observed visually, and the thickness of the metal Cu on the front face of a wafer was measured further. A result is shown in Table 8. In addition, -in Table 8 shows measurement impossible.

[0106]

[Table 7]

[0107]  
[Table 8]

[0108] When a wafer is washed using the cleaning agent (metal corrosion inhibitor) (examples 35-44) of this invention so that clearly from Table 7 and 8, the residual Cu concentration on the front face of a wafer can be controlled for 1010 or less \*\*\*\*\*s, and it is changeless to the color tone of Cu film front face, and Metal Cu does not oxidize, and there is almost no change in Cu thickness, and it turns out that Metal Cu is not being corroded. On the other hand, although residual Cu concentration can be controlled for 1010 or less \*\*\*\*\*s when the cleaning agent of the examples 27, 30, 31, 33, and 34 of a comparison is used, Metal Cu oxidizes and it turns out that Metal Cu is being corroded remarkably. Moreover, although the metal Cu on the front face of a wafer does not oxidize and corrosion is hardly carried out for Metal Cu, either, when the example 29 of a comparison and the cleaning agent of 35-37 are used, residual Cu concentration is high and it turns out that the copper oxide on the front face of a wafer cannot fully be removed. Furthermore, when the cleaning agent of the examples 26 and 32 of a comparison is used, Metal Cu corrodes and oxidizes, and residual Cu concentration is high, and it turns out that the copper oxide on the front face of a wafer cannot fully be removed. When the cleaning agent of the example 28 of a comparison is

used, it turns out that Metal Cu is being corroded remarkably and the copper oxide on the front face of a wafer cannot fully be removed. That is, if the substrate front face which has the metallic-coating section on a front face using the cleaning agent of this invention is washed, it turns out that oxidation and corrosion of the metal concerned can be prevented and the metal impurity (copper oxide) of the front face concerned can be removed effectively.

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(54) 【発明の名称】 基板洗浄剤

(57) 【要約】 (修正有)

【課題】 特に表面に銅配線が施された基板表面の洗浄剤に添加して、銅配線の腐食や酸化を起こさず、表面の金属不純物（酸化銅）を有効に除去し得る金属腐食防止剤を提供する。

【解決手段】 例えばシステインのような、分子内にチオール基を有するアミノ酸、又はN-アセチルシステインのような、アミノ酸のN-アシル体、システインメチルエステルのようなアミノ酸のカルボン酸エステル体などのアミノ酸誘導体を含んでなる金属腐食防止剤を添加する。

【特許請求の範囲】

【請求項 1】分子内にチオール基を有するアミノ酸又はその誘導体を含んでなる金属腐蝕防止剤。

【請求項 2】水性溶液である請求項 1 に記載の金属腐蝕防止剤。

【請求項 3】分子内にチオール基を有するアミノ酸が、システイン又はホモシステインである請求項 1 又は 2 に記載の金属腐蝕防止剤。

【請求項 4】アミノ酸誘導体がアミノ酸の N-アシル体又はアミノ酸のカルボン酸エステル体である請求項 1 ~ 3 の何れかに記載の金属腐蝕防止剤。

【請求項 5】N-アシル体がカルボン酸由来のアシル基が導入されたものである請求項 4 に記載の金属腐蝕防止剤。

【請求項 6】N-アシル体が N-アルカノイル体又は N-アラルカノイル体である請求項 4 に記載の金属腐蝕防止剤。

【請求項 7】N-アシル体が N-アセチル体である請求項 4 に記載の金属腐蝕防止剤。

【請求項 8】エステル体がアルキルエステル体又はアラルキルエステル体である請求項 4 に記載の金属腐蝕防止剤。

【請求項 9】エステル体が低級アルキルエステル体又はベンジルエステル体である請求項 4 に記載の金属腐蝕防止剤。

【請求項 10】更に、有機酸、アミン、無機アルカリ化合物、キレート剤及び界面活性剤のうちの少なくとも一つを含んでなる請求項 1 ~ 9 の何れかに記載の金属腐蝕防止剤。

【請求項 11】有機酸がジ乃至トリカルボン酸である請求項 10 に記載の金属腐蝕防止剤。

【請求項 12】有機酸がモノ乃至ジヒドロキシジ乃至トリカルボン酸である請求項 10 に記載の金属腐蝕防止剤。

【請求項 13】アミンが、アルキルアミン、ジアルキルアミン、ヒドロキシアルキルアミン、アルキレンジアミン、ジアルキレントリアミン、トリアルキレンテトラミン、アルキルアミン-アルキレンオキサイド付加物、テトラアルキルアンモニウムヒドロキシドの何れかである請求項 10 に記載の金属腐蝕防止剤。

【請求項 14】無機アルカリ化合物が、窒素含有無機アルカリ化合物である請求項 10 に記載の金属腐蝕防止剤。

【請求項 15】窒素含有無機アルカリ化合物が、ヒドロキシルアミン、ヒドラジン、アンモニア、及びこれらの塩からなる群より選ばれるものである請求項 14 に記載の金属腐蝕防止剤。

【請求項 16】キレート剤がアミノポリカルボン酸類又はノ及びホスホン酸類である請求項 10 に記載の金属腐蝕防止剤。

【請求項 17】アミノポリカルボン酸類が、直鎖型アミ

ノポリカルボン酸類又はノ及び環状アミノポリカルボン酸類である請求項 16 に記載の金属腐蝕防止剤。

【請求項 18】直鎖型アミノポリカルボン酸類が、EDTA（エチレンジアミン四酢酸）、EDDA（エチレンジアミン二酢酸）、EDTA-OH（ヒドロキシエチレンジアミン三酢酸）、GEDTA（グリコールエーテルジアミン四酢酸）、DTPA（ジエチレントリアミン五酢酸）、IDA（イミノジ酢酸）、methyl-EDTA（ジアミノプロパン四酢酸）、NTA（ニトリロ三酢酸）、TTHA（トリエチレンテトラミン六酢酸）、またはそのアンモニウム塩若しくはアミンとの錯塩である請求項 17 に記載の金属腐蝕防止剤。

【請求項 19】環状アミノポリカルボン酸類が、CyDTA（trans-シクロヘキシルジアミノ四酢酸）、またはそのアンモニウム塩若しくはアミンとの錯塩である請求項 17 に記載の金属腐蝕防止剤。

【請求項 20】ホスホン酸類が、ポリホスホン酸類又はノ及びアミノポリホスホン酸類である請求項 16 に記載の金属腐蝕防止剤。

【請求項 21】ポリホスホン酸類が、NTPO（ニトリロトリスメチレンホスホン酸）、HEDPO（ヒドロキシエチリデンジ（メチレンホスホン酸））、またはそのアンモニウム塩若しくはアミンとの錯塩である請求項 20 に記載の金属腐蝕防止剤。

【請求項 22】アミノポリホスホン酸類が、EDDPO（エチレンジアミンジ（メチレンホスホン酸））、EDTPO（エチレンジアミンテトラ（メチレンホスホン酸））、PDTPPO（ジアミノプロパンテトラ（メチレンホスホン酸））、DETPPO（ジエチレントリアミンペンタ（メチレンホスホン酸））、TTHPO（トリエチレンテトラミンヘキサ（メチレンホスホン酸））またはそのアンモニウム塩若しくはアミンとの錯塩である請求項 20 に記載の金属腐蝕防止剤。

【請求項 23】界面活性剤が、ノニオン系界面活性剤またはアニオン系界面活性剤である請求項 10 に記載の金属腐蝕防止剤。

【請求項 24】ノニオン系界面活性剤が、分子中にポリオキシアルキレン基を有するものである請求項 23 に記載の金属腐蝕防止剤。

【請求項 25】ノニオン系界面活性剤が、ポリオキシアルキレンアルキルエーテル類又はポリオキシアルキレンポリアルキルアリアルエーテル類である請求項 23 に記載の金属腐蝕防止剤。

【請求項 26】アニオン系界面活性剤が、スルホン酸基、カルボキシル基、ホスホン酸基及びスルホキシル基からなる群より選ばれる基を有するものである請求項 23 に記載の金属腐蝕防止剤。

【請求項 27】アニオン系界面活性剤が、アルキルスルホン酸、アルキルアリアルスルホン酸、アルキル硫酸エステル、アルキルアリアル硫酸エステル、ポリオキシ



ルキレンアルキル硫酸エステル、ポリオキシアルキレンアルキルアリール硫酸エステル、アルキルカルボン酸、アルキルアリールカルボン酸、又はこれらの塩である請求項 26 に記載の金属腐蝕防止剤。

【請求項 28】請求項 1～27 の何れかに記載の金属腐蝕防止剤を含んでなる処理剤。

【請求項 29】処理剤が表面に銅被覆部を有する基板用である請求項 28 に記載の処理剤。

【請求項 30】基板が半導体基板である請求項 29 に記載の処理剤。

【請求項 31】基板を請求項 28 に記載の処理剤で処理することを特徴とする該基板の処理方法。

【請求項 32】基板が表面に銅被覆部を有するものである請求項 31 に記載の処理方法。

【請求項 33】基板が半導体基板である請求項 32 に記載の処理方法。

【請求項 34】請求項 1～27 の何れかに記載の金属腐蝕防止剤を含んでなる洗浄剤。

【請求項 35】洗浄剤が表面に銅被覆部を有する基板用である請求項 34 に記載の洗浄剤。

【請求項 36】基板が半導体基板である請求項 34 に記載の洗浄剤。

【請求項 37】基板を請求項 34 に記載の洗浄剤で洗浄することを特徴とする該基板の洗浄方法。

【請求項 38】基板が表面に銅被覆部を有する半導体基板である請求項 37 に記載の洗浄方法。

【請求項 39】基板が半導体基板である請求項 38 に記載の洗浄方法。

【請求項 40】表面に銅被覆部を有する半導体基板を化学的物理的研磨処理 (CMP) に付した後、当該基板を請求項 28 に記載の処理剤で処理することを特徴とする該基板の処理方法。

【請求項 41】表面に銅被覆部を有する半導体基板を化学的物理的研磨処理 (CMP) に付した後、当該基板を請求項 28 に記載の処理剤で処理し、次いで当該基板を半導体基板洗浄剤で洗浄することを特徴とする該基板の処理方法。

【請求項 42】表面に銅被覆部を有する半導体基板を化学的物理的研磨処理 (CMP) に付した後、当該基板を請求項 34 に記載の洗浄剤で洗浄することを特徴とする該基板の洗浄方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、金属腐蝕防止剤、及びこれを用いた基板表面、特に、表面に銅配線が施された基板表面の洗浄剤及び洗浄方法に関する。

【0002】

【従来の技術】近年、LSIの構造は、高集積化に伴い微細化が進んでおり、半導体表面に金属配線などが幾段にも重ねられた多層構造となっている。また、使用される

配線も従来のアルミニウムから、より電氣的抵抗の低い銅 (Cu) への変更が提案されている。

【0003】表面に銅配線が多層に亘って施された多層構造を有する半導体を製造する工程には、金属Cuを酸化しながら物理的に半導体基板を研磨して平坦化するいわゆる化学的物理的研磨技術 (Cu-CMP) が利用される。

【0004】一方、Cu-CMP工程後の半導体表面には、Cu配線とそれぞれのCu配線を隔離する絶縁膜 (酸化ケイ素) が剥き出しの状態となっており、Cu-CMP工程後のウエーハ表面は多量の金属不純物により汚染されている。金属不純物汚染はCMPによって削り取られるCuが絶縁膜上の吸着し金属酸化物 (酸化銅) として残存することに起因している。

【0005】このように絶縁膜上に金属酸化物 (酸化銅) が残存すると、後工程での熱処理で銅元素が絶縁膜中に拡散し、絶縁性が低下することでデバイスの特性が劣化してしまい、汚染が著しい場合は、隔離した配線同士が結線、即ち、ショートを起こしてしまうため、デバイスが破壊されてしまう。そのため、次工程に進む前に、金属酸化物 (酸化銅) を除去する必要がある。

【0006】以上の理由で、上記した如き金属不純物を除去するために、Cu-CMP工程後の洗浄工程は必須である。

【0007】一方、半導体表面の金属銅は、活性が高く、僅かな酸化力によって容易に腐蝕されて、配線抵抗が増大したり、断線を引き起こしてしまう。このため、Cu-CMP工程後の洗浄工程に於いては、従来、半導体用の洗浄液として用いられている、比較的酸化力の強い、塩酸やフッ酸等の無機酸を主成分とする洗浄液を用いると、絶縁膜上に付着した酸化銅のみならず、配線の金属銅をも溶解してしまうので、当該酸性洗浄液の使用は好ましくない。また、シュウ酸やクエン酸等の比較的酸化力の弱い有機酸を主成分とする洗浄剤も、無機酸に比べて銅の溶解作用は弱いものの、銅溶解作用を有しているため、極力低濃度の有機酸を使用する必要があった。このため、有機酸を低濃度で使用した場合には、金属酸化物の溶解力も低下してしまうため、半導体表面を長時間に亘り洗浄する必要があった。

【0008】このような欠点を解消するために、洗浄剤に種々の金属腐蝕防止剤を添加することにより、半導体表面上の金属銅の腐蝕を防止し得ることが知られている。

【0009】例えば特開平7-79061号公報等には、ベンゾトリアゾール類やイミダゾール類を代表とする芳香族系化合物が開示されている。しかしながら、これら化合物は、銅の腐食防止効果が低く、高濃度でしか防止効果が認められない。しかしながら、当該化合物は、水への溶解度が低く、半導体用洗浄剤を使用する際に希釈液として一般に用いられる超純水中に、これら化合物を高濃度で添加することは困難であった。また、こ

れら化合物を高濃度で使用するには、アミン等のアルカリ可溶化剤やアルコール系の有機溶剤等が必要となるが、これら可溶化剤や有機溶剤は、洗浄特性に悪影響を及ぼすため、使用が困難であった。

【0010】また、特開2000-87268号公報や特開2000-282096号公報等には、メルカプトイミダゾールやメルカプトチアゾール等の環状化合物が開示されている。しかしながら、これら化合物は、半導体表面の銅と結合すると、銅表面が疎水性となり、洗浄剤の攻撃を阻止するので、これら化合物を除去するのが困難となる。このように、これらの化合物のような有機物が銅表面に残存したまま、後の工程やデバイス作動時等に於いて半導体が熱処理を受けると、当該有機物が燃焼、爆発等し、重大な欠陥が生じてしまうという問題や、毒性が強く、人体や環境に対する安全性等に問題があった。

【0011】更に、特開2000-273663号公報には、メルカプトエタノールやメルカプトグリセロール等の、分子中にメルカプト基を有し且つ当該メルカプト基が結合している炭素と水酸基が結合している炭素とが隣接して結合している脂肪族アルコール系化合物が開示されている。しかしながら、特開2000-273663号公報に開示された発明は、近年の人体への影響や環境汚染等に関する問題から、従来のものに比べて人の健康や生態系に有害な影響を与える恐れが少ない金属腐蝕防止剤を提供することを目的としてなされたものであるが、毒性は強く、未だ安全性に問題があり、また、これら化合物は、蒸気圧が比較的低く、水溶液中に添加して使用した場合でも不快臭があり、実用的ではない。

【0012】

【発明が解決しようとする課題】本発明は、上記した如き状況に鑑みなされたもので、良好な金属腐蝕防止作用を有し且つ安全性が高い金属腐蝕防止剤、及びこれを用いた、基板表面、特に、表面に銅配線が施された基板表面に於ける銅配線の酸化や腐蝕を防止し得る当該基板の処理方法、並びに、当該基板表面の銅配線の腐蝕や酸化を防止し得、且つ当該表面の金属不純物（酸化銅）を有効に除去し得る基板の洗浄方法を提供するものである。

【0013】

【課題を解決するための手段】本発明は、以下の構成よりなる。

【0014】(1) 分子内にチオール基を有するアミノ酸又はその誘導体を含んでなる金属腐蝕防止剤。

【0015】(2) 上記(1)に記載の金属腐蝕防止剤を含んでなる処理剤。

【0016】(3) 基板を上記(2)に記載の処理剤で処理することを特徴とする該基板の処理方法。

【0017】(4) 上記(1)に記載の金属腐蝕防止剤を含んでなる洗浄剤。

【0018】(5) 基板を上記(4)に記載の洗浄剤で

洗浄することを特徴とする該基板の洗浄方法。

【0019】(6) 表面に銅被覆部を有する半導体基板を化学的物理的研磨処理(CMP)に付した後、当該基板を上記(2)に記載の処理剤で処理することを特徴とする該基板の処理方法。

【0020】(7) 表面に銅被覆部を有する半導体基板を化学的物理的研磨処理(CMP)に付した後、当該基板を上記(2)に記載の処理剤で処理し、次いで当該基板を半導体基板洗浄剤で洗浄することを特徴とする該基板の処理方法。

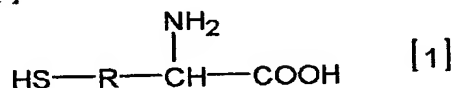
【0021】(8) 表面に銅被覆部を有する半導体基板を化学的物理的研磨処理(CMP)に付した後、当該基板を上記(4)に記載の洗浄剤で洗浄することを特徴とする該基板の洗浄方法。

【0022】本発明者等は上記目的を達成すべく鋭意研究を重ねた結果、分子内にチオール基を有するアミノ酸又はその誘導体が、良好な金属腐蝕防止作用を有し且つ安全性が高いこと、並びに当該アミノ酸又はその誘導体を含有する洗浄剤を用いて基板を処理すれば、基板表面、特に、表面に銅配線が施された基板表面を、銅配線の腐蝕や酸化を起こさず、当該表面の金属不純物（酸化銅）を有効に除去し得ることを見出し、本発明を完成させるに至った。

【0023】本発明に係る分子内にチオール基を有するアミノ酸（以下、本発明に係るアミノ酸と略記する場合がある。）は、分子内にチオール基、カルボキシル基及びアミノ基を有するものであり、具体的には下記一般式【1】で示される化合物が挙げられる。

【0024】

【化1】



【0025】(式中、Rは低級アルキレン基を示す。)

【0026】一般式【1】に於いて、Rで示される低級アルキレン基としては、例えばメチレン基、エチレン基、トリメチレン基、テトラメチレン基、ペンタメチレン基、ヘキサメチレン基、プロピレン基、ブチレン基、メチルメチレン基、エチルエチレン基、メチルエチレン基、メチルプロピレン基、エチルプロピレン基、ペンチレン基、ヘキシレン基、シクロペンチレン基、シクロヘキシレン基等の直鎖状、分枝状あるいは環状の炭素数1～6の低級アルキレン基が挙げられる。なかでも、炭素数1～6の直鎖状のアルキレン基（メチレン基、エチレン基、トリメチレン基、テトラメチレン基、ペンタメチレン基、ヘキサメチレン基）が好ましく、メチレン基又はエチレン基が特に好ましい。

【0027】本発明に係る分子内にチオール基を有するアミノ酸は、市販品（例えば和光純薬工業（株）製）を用いてもよいし、自体公知の方法に準じて適宜調製して

用いてもよい。

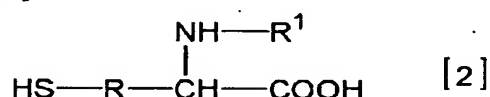
【0028】上記一般式〔1〕で示される化合物としては、より具体的には、例えばシステイン、ホモシステイン等が挙げられ、これらはD体でもL体でも、DL体でも、また、夫々混合比が異なるD体とL体との混合物でも使用可能である。

【0029】上記した如き、本発明に於ける分子内にチオール基を有するアミノ酸の誘導体としては、金属腐食防止作用を有するものであれば特に限定されないが、例えば本発明に係るアミノ酸のN-アシル体又は本発明に係るアミノ酸のカルボン酸エステル体等が挙げられる。

【0030】本発明に係るアミノ酸のN-アシル体とは、上記した如き本発明に係るアミノ酸が有するアミノ基の水素原子にアシル基が導入されたものである。具体的には、下記一般式〔2〕に示すように、上記一般式〔1〕に於けるアミノ基の水酸基にアシル基が導入されたものである。

【0031】

〔化2〕



【0032】(式中、 $\text{R}^1$  はアシル基を示し、Rは前記と同じ。)

【0033】本発明に係るアミノ酸が有するアミノ基の水素原子に導入されるアシル基又は一般式〔2〕に於いて $\text{R}^1$ で示されるアシル基としては、直鎖状、分枝状或いは環状でもよく、例えばホルミル基、アセチル基、プロピオニル基、ブチリル基、イソブチリル基、バレリル基、イソバレリル基、ピバロイル基、ヘキサノイル基、シクロプロピオニルカルボニル基、シクロペンチルカルボニル基、シクロヘキシルカルボニル基等の炭素数1～6の飽和脂肪族モノカルボン酸由来のもの、例えばアクリロイル基、プロピオロイル基、メタクリロイル基、クロトノイル基、イソクロトノイル基等の炭素数3～7の不飽和脂肪族モノカルボン酸由来のもの、例えばベンゾイル基、ナフトイル基、ベンタレンカルボニル基、インデレンカルボニル基、アズレンカルボニル基、ヘプタレンカルボニル基、インダセンカルボニル基、アントラセンカルボニル基、フェナントレンカルボニル基、トリフェニレンカルボニル基、ピレンカルボニル基、ナフタセンカルボニル基、ピリレンカルボニル基、ペンタセンカルボニル基等の炭素数7～23、好ましくは炭素数7～12の芳香族モノカルボン酸由来のもの、例えばフェニルメチルカルボニル基、フェニルエチルカルボニル基、フェニルプロピルカルボニル基、フェニルイソプロピルカルボニル基、フェニルブチルカルボニル基、フェニルイソブチルカルボニル基、フェニルペンチルカルボニル基、フェニルネオペンチルカルボニル基、フェニルヘキシルカルボニル基、フ

エニルイソヘキシルカルボニル基、フェニルエチルペンチルカルボニル基、フェニルメチルペンチルカルボニル基、フェニルジメチルブチルカルボニル基、フェニルエチルブチルカルボニル基、フェニルヘブチルカルボニル基、フェニルメチルヘキシルカルボニル基、フェニルジメチルペンチルカルボニル基、フェニルオクチルカルボニル基、フェニルノニルカルボニル基、フェニルデシルカルボニル基、フェニルウンデシルカルボニル基、フェニルドデシルカルボニル基、フェニルトリデシルカルボニル基、フェニルシクロプロピルカルボニル基、フェニルシクロペンチルカルボニル基、フェニルシクロヘキシルカルボニル基、フェニルシクロヘキシルカルボニル基、フェニルシクロヘブチルカルボニル基、フェニルシクロオクチルカルボニル基、フェニルシクロノニルカルボニル基、フェニルシクロデシルカルボニル基、フェニルシクロウンデシルカルボニル基、フェニルシクロドデシルカルボニル基、フェニルシクロトリデシルカルボニル基、等の炭素数7～20、好ましくは炭素数7～13のアラルキルモノカルボン酸由来のもの等が挙げられる。

尚、上記した如き芳香族モノカルボン酸由来のアシル基又はアラルキルモノカルボン酸由来のアシル基の芳香環には、例えばメチル基、エチル基等の低級アルキル基等を置換基として有していてもよい。上記した如きアシル基のなかでも、飽和脂肪族モノカルボン酸由来のもの及びアラルキルモノカルボン酸由来のものが好ましく、より好ましくは飽和脂肪族モノカルボン酸由来のものであり、更に好ましくは直鎖状の飽和脂肪族モノカルボン酸由来のものである。直鎖状の飽和脂肪族モノカルボン酸由来のアシル基のなかでも、アセチル基が特に好ましい。

【0034】また、本発明に係る分子内にチオール基を有するアミノ酸のN-アシル体は、市販品(例えば和光純薬工業(株)製)を用いてもよいし、自体公知の方法に準じて適宜調製して用いてもよい。

【0035】本発明に係るアミノ酸のN-アシル体としては、本発明に係るアミノ酸が有するアミノ基の水素原子に、飽和脂肪族モノカルボン酸由来のアシル基が導入されたN-アルカノイル体(一般式〔2〕に於ける $\text{R}^1$ が飽和脂肪族モノカルボン酸由来のアシル基であるもの)及びアラルキルモノカルボン酸由来のアシル基が導入されたN-アラルカノイル体(一般式〔2〕に於ける $\text{R}^1$ がアラルキルモノカルボン酸由来のアシル基であるもの)が好ましく、より好ましくはN-アルカノイル体であり、更に好ましくは、本発明に係るアミノ酸が有するアミノ基の水素原子に、直鎖状の飽和脂肪族モノカルボン酸由来のアシル基が導入されたN-直鎖アルカノイル体(一般式〔2〕に於ける $\text{R}^1$ が直鎖状の飽和脂肪族モノカルボン酸由来のアシル基であるもの)である。なかでも、本発明に係るアミノ酸が有するアミノ基の水素原子に、アセチル基が導入されたN-アセチル体(一般式〔2〕に於け

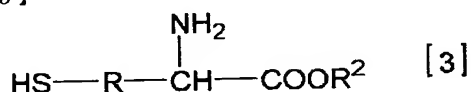
るR<sup>1</sup>がアセチル基であるもの)が特に好ましい。本発明に係るアミノ酸のN-アシル体(一般式[2]で示される化合物)の具体例としては、例えばN-アセチルシステイン、N-ブチリルシステイン、N-シクロヘキシルカルボニルシステイン、N-プロピオロイルシステイン、N-クロトノイルシステイン、N-ベンゾイルシステイン、N-ナフトイルシステイン、N-フェニルメチルカルボニルシステイン、N-フェニルブチルカルボニルシステイン、N-フェニルシクロヘキシルカルボニルシステイン、N-アセチルホモシステイン、N-ブチリルホモシステイン、N-シクロヘキシルカルボニルホモシステイン、N-プロピオロイルホモシステイン、N-クロトノイルホモシステイン、N-ベンゾイルホモシステイン、N-ナフトイルホモシステイン、N-フェニルメチルカルボニルホモシステイン、N-フェニルブチルカルボニルホモシステイン、N-フェニルシクロヘキシルカルボニルホモシステイン等が挙げられ、これらはD体でもL体でも、DL体でも、また、夫々混合比が異なるD体とL体との混合物でも使用可能である。

【0036】本発明に係るアミノ酸のカルボン酸エステル体とは、上記した如き本発明に係るアミノ酸が有するカルボキシル基がエステル化されたものである。具体的には、下記一般式[2]に示すように、上記一般式

[1]に於けるカルボキシル基の水酸基にアシル基が導入されたものである。

【0037】

【化3】



【0038】(式中、R<sup>2</sup>は炭化水素残基を示し、Rは前記と同じ。)

【0039】一般式[3]に於いて、R<sup>2</sup>で示される炭化水素残基としては、一価の基であれば、脂肪族、芳香族、芳香脂肪族、或いは脂環族の何れでもよく、また、脂肪族及び芳香脂肪族に於ける脂肪族としては、飽和でも不飽和でも、また、直鎖状でも分枝状でもよい。これらのうちの代表的なものとしては、例えば直鎖状、分枝状、或いは環状の飽和又は不飽和のアルキル基、アリール基、アラルキル基、アルケニル基等が挙げられる。アルキル基としては、通常炭素数1~10のもの、好ましくは1~6のもの、より好ましくは1~4のものが挙げられ、具体的には、例えばメチル基、エチル基、n-プロピル基、iso-プロピル基、n-ブチル基、iso-ブチル基、sec-ブチル基、tert-ブチル基、n-ペンチル基、iso-ペンチル基、sec-ペンチル基、tert-ペンチル基、ネオペンチル基、n-ヘキシル基、iso-ヘキシル基、3-メチルペンチル基、2-メチルペンチル基、1,2-ジメチルブチル基、sec-ヘキシル基、tert-ヘキシル基、n-ヘプチル基、iso-ヘプチル基、sec-ヘプチル基、n-オクチル基、

iso-オクチル基、sec-オクチル基、n-ノニル基、n-デシル基、シクロプロピル基、シクロペンチル基、シクロヘキシル基、シクロヘプチル基、シクロオクチル基、シクロデシル基等が挙げられる。アリール基としては、通常炭素数6~14のものが挙げられ、具体的には、例えばフェニル基、o-トリル基、m-トリル基、p-トリル基、2,3-キシリル基、2,4-キシリル基、2,5-キシリル基、2,6-キシリル基、3,5-キシリル基、ナフチル基、アントリル基等が挙げられる。アラルキル基としては、通常炭素数7~12のもの、好ましくは7~10のものが挙げられ、具体的には、例えばベンジル基、フェネチル基、フェニルプロピル基、フェニルブチル基、フェニルヘキシル基、メチルベンジル基、メチルフェネチル基、エチルベンジル基等が挙げられる。

尚、上記した如きアリール基又はアラルキル基の芳香環には、例えばメチル基、エチル基等の低級アルキル基や、ハロゲン原子、ニトロ基、アミノ基等を置換基として有していてもよい。アルケニル基としては、通常2~10のものが挙げられ、具体的には、例えばビニル基、アリル基、1-プロペニル基、iso-プロペニル基、3-ブテニル基、2-ブテニル基、1-ブテニル基、1,3-ブタジエニル基、4-ペンテニル基、3-ペンテニル基、2-ペンテニル基、1-ペンテニル基、1,3-ペンタジエニル基、2,4-ペンタジエニル基、1,1-ジメチル-2-プロペニル基、1-エチル-2-プロペニル基、1,2-ジメチル-1-プロペニル基、1-メチル-1-ブテニル基、5-ヘキセニル基、4-ヘキセニル基、2-ヘキセニル基、1-ヘキセニル基、1-メチル-1-ヘキセニル基、2-メチル-2-ヘキセニル基、3-メチル-1,3-ヘキサジエニル基、1-ヘプタニル基、2-オクテニル基、3-ノネニル基、4-デセニル基、2-シクロペンテニル基、2,4-シクロペンタジエニル基、1-シクロヘキセニル基、2-シクロヘキセニル基、3-シクロヘキセニル基、2-シクロヘプテニル基、2-シクロノネニル基、3-シクロデセニル基等が挙げられる。なかでも、アルキル基及びアラルキル基が好ましく、より好ましくは炭素数1~6の低級アルキル基及びベンジル基であり、更に好ましくは炭素数1~6の低級アルキル基である。

【0040】本発明に係る分子内にチオール基を有するアミノ酸のカルボン酸エステル体は、市販品(例えば和光純薬工業(株)製)を用いてもよいし、自体公知の方法に準じて適宜調製して用いてもよい。

【0041】本発明に係るアミノ酸のカルボン酸エステル体としては、本発明に係るアミノ酸が有するカルボキシル基に、アルキル基が導入されたアルキルエステル体(一般式[3]に於けるR<sup>2</sup>がアルキル基であるもの)及びアラルキル基が導入されたアラルキルエステル体(一般式[3]に於けるR<sup>2</sup>がアラルキル基であるもの)が好ましく、より好ましくは本発明に係るアミノ酸が有するカルボキシル基に、炭素数1~6のアルキル基が導入された低級アルキルエステル体(一般式[3])

に於ける $R^2$ が炭素数1～6の低級アルキル基であるもの)及びベンジル基が導入されたベンジルエステル体(一般式[3]に於ける $R^2$ がベンジル基であるもの)であり、更に好ましくは、低級アルキルエステル体である。本発明に係るアミノ酸のカルボン酸エステル体(一般式[3]で示される化合物)の具体例としては、例えばシステインメチルエステル、システインエチルエステル、システインイソブチルエステル、システイン*n*-ヘキシルエステル、システインシクロヘキシルエステル、システインフェニルエステル、システインナフチルエステル、システインベンジルエステル、システインメチルベンジルエステル、システインビニルエステル、システイン3-ブテニルエステル、システイン3-シクロヘキセニルエステル、ホモシステインメチルエステル、ホモシステインエチルエステル、ホモシステインイソブチルエステル、ホモシステイン*n*-ヘキシルエステル、ホモシステインシクロヘキシルエステル、ホモシステインフェニルエステル、ホモシステインナフチルエステル、ホモシステインベンジルエステル、ホモシステインメチルベンジルエステル、ホモシステインビニルエステル、ホモシステイン3-ブテニルエステル、ホモシステイン3-シクロヘキセニルエステル等が挙げられ、これらはD体でもL体でも、DL体でも、また、夫々混合比が異なるD体とL体との混合物でも使用可能である。

【0042】上記した如き本発明に係る分子内にチオール基を有するアミノ酸又はその誘導体は、単独で使用しても、2種以上適宜組み合わせて用いてもよい。

【0043】分子内にチオール基を有するアミノ酸又はその誘導体の使用量は、分子内にチオール基を有するアミノ酸又はその誘導体の種類や処理される基板の表面積等によって異なるため一概には言えないが、例えば通常0.0001～10重量%、好ましくは0.0001～1重量%、より好ましくは0.0001～0.5重量%である。

【0044】本発明の金属腐蝕防止剤は、上記した如き本発明に係る分子内にチオール基を有するアミノ酸又はその誘導体を含んでなるものである。また、本発明の金属腐蝕防止剤は、通常水性溶液の状態であり、当該本発明に係るアミノ酸又はその誘導体を水に添加溶解させることにより調製される。

【0045】本発明に係るアミノ酸又はその誘導体を水に溶解する方法としては、例えば水の中に別途溶解した本発明に係るアミノ酸又はその誘導体を添加する方法や、本発明に係るアミノ酸又はその誘導体を直接水に添加し、溶解、攪拌する方法等が挙げられる。

【0046】このようにして調製した本発明の金属腐蝕防止剤は、使用前に濾過処理等を行うのが好ましい。また、ここで用いられる水は、蒸留、イオン交換処理等により精製されたものであればよいが、この分野で用いられる、いわゆる超純水がより好ましい。

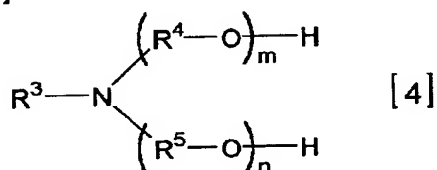
【0047】更に本発明に係る金属腐蝕防止剤中には、

上記した如き本発明に係るアミノ酸又はその誘導体以外に、通常この分野で用いられる試薬類を使用することができる。このような試薬類としては、例えば有機酸、アミン、無機アルカリ化合物、キレート剤、界面活性剤等である。

【0048】本発明に於いて用いられる有機酸としては、通常この分野で用いられるものであればよく、特に限定されないが、例えばシュウ酸、マロン酸、コハク酸、グルタル酸、アジピン酸、ピメリン酸、スベリン酸、2-*n*-ブチルマロン酸、マレイン酸、フマル酸、シトラコン酸、メサコン酸、フタル酸、イソフタル酸、テレフタル酸等の炭素数2～8のジカルボン酸、例えばトリカルバリル酸、ベンゼントリカルボン酸等の炭素数6以上のトリカルボン酸、例えばタルトロン酸、リンゴ酸等の炭素数3以上のモノヒドロキシジカルボン酸、例えば酒石酸等の炭素数4以上のジヒドロキシジカルボン酸、例えばクエン酸等の炭素数6以上のモノヒドロキシトリカルボン酸、例えばヒドロキシトリカルボン酸、これらのアンモニウム塩等が挙げられる。なかでも、ジカルボン酸、モノヒドロキシジカルボン酸、モノヒドロキシトリカルボン酸及びジヒドロキシジカルボン酸が好ましく、ジカルボン酸及びモノヒドロキシトリカルボン酸が特に好ましい。より具体的には、シュウ酸、マロン酸、フタル酸、リンゴ酸、クエン酸、酒石酸が好ましく、クエン酸、シュウ酸が特に好ましい。また、これら有機酸は、単独で使用しても、2種以上適宜組み合わせ用いてもよい。有機酸の使用量は、有機酸の種類によって異なるため一概には言えないが、例えば通常0.0001～20重量%、好ましくは0.001～10重量%、より好ましくは0.05～10重量%である。

【0049】本発明に於いて用いられるアミンとしては、通常この分野で用いられるものであればよく、特に限定されないが、例えばメチルアミン、エチルアミン、*n*-プロピルアミン、*n*-ブチルアミン、*n*-ペンチルアミン、*n*-ヘキシルアミン、シクロペンチルアミン、シクロヘキシルアミン等の炭素数1～6のアルキルアミン、例えばジメチルアミン、メチルエチルアミン、ジエチルアミン、ジプロピルアミン等の炭素数2～12、好ましくは炭素数2～6のジアルキルアミン、例えばトリメチルアミン、ジメチルエチルアミン、メチルジエチルアミン、トリエチルアミン、トリプロピルアミン等の炭素数3～18、好ましくは炭素数3～6のトリアルキルアミン、例えばモノエタノールアミン、ジエタノールアミン、トリエタノールアミン、ジメチルエタノールアミン、ジエチルエタノールアミン等の炭素数1～18、好ましくは炭素数1～6のモノ乃至トリヒドロキシアルキルアミン、例えばメチレンジアミン、エチレンジアミン、プロピレンジアミン、イソプロピレンジアミン、ブチレンジアミン、メチルメチレンジアミン、エチルエチレンジアミン、メチルエチレンジアミン、メチルプロピ

【化4】



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[illegible]

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【0052】上記した如きアミンのなかでも、アルキレンジアミン、ジアルキレントリアミン、トリアルキレンテトラミン、アルキルアミン-アルキレンオキサイド付加物、テトラアルキルアンモニウムヒドロキシドが好ましく、なかでもアルキレンジアミン、シクロアルキルアミンジ(ポリオキシアルキレン)が特に好ましい。具体的には、エチレンジアミン、ジエチレントリアミン、トリエチレンテトラミン、シクロヘキシルアミンジ(ポリオキシエチレン)、シクロヘキシルアミン(ポリオキシエチレン)(ポリオキシメチレン)、テトラメチルアンモニウムヒドロキシドが好ましく、なかでもエチレンジアミン、シクロヘキシルアミンジ(ポリオキシエチレン)が特に好ましい。また、これらアミンは、単独で使用しても、2種以上適宜組み合わせ用いてもよい。アミンの使用量は、アミンの種類によって異なるため一概には言えないが、例えば通常0.0001~20重量%、好ましくは0.001~10重量%、より好ましくは0.05~10重量%である。

【0053】本発明に於いて用いられる無機アルカリ化合物としては、通常この分野で用いられるものであればよく、特に限定されないが、例えばヒドロキシアミン、ヒドラジン、アンモニア、これらの塩(例えば塩酸塩、硫酸塩等)等の窒素含有無機アルカリ化合物、例えば水酸化カリウム、水酸化ナトリウム等の無機アルカリ等が挙げられる。なかでも、窒素含有無機アルカリ化合物が

好ましく、特に、金属を含まない窒素含有無機アルカリ化合物が好ましい。具体的にはヒドロキシアミン、ヒドラジン及びアンモニアが好ましく、特に、アンモニアが好ましい。また、これら無機アルカリ化合物は、単独で使用しても、2種以上適宜組み合わせ用いてもよい。無機アルカリ化合物の使用量は、無機アルカリ化合物の種類によって異なるため一概には言えないが、例えば通常0.0001~20重量%、好ましくは0.001~10重量%、より好ましくは0.05~10重量%である。

【0054】本発明に於いて用いられるキレート剤としては、通常この分野で用いられるものであればよく、特に限定されない。キレート剤を添加することにより、液中に分散した酸化銅等の金属酸化物を可溶化し、再吸着を抑えることができ、また、FeやAl等の不純物を基板表面から除去することもできる。このようなキレート剤としては、例えばEDTA(エチレンジアミン四酢酸)、EDDA(エチレンジアミン二酢酸)、EDTA-OH(ヒドロキシエチレンジアミン三酢酸)、GEDTA(グリコールエーテルジアミン四酢酸)、DTPA(ジエチレントリアミン五酢酸)、IDA(イミノジ酢酸)、methyl-EDTA(ジアミノプロパン四酢酸)、NTA(ニトリロ三酢酸)、TTHA(トリエチレンテトラミン六酢酸)、これらのアンモニウム塩、これらとアミンとの錯塩等の直鎖型アミノポリカルボン酸類、例えばCyDTA(trans-シクロヘキシルジアミノ四酢酸)、これのアンモニウム塩、これとアミンとの錯塩等の環状アミノポリカルボン酸類等のアミノポリカルボン酸類、例えばNTPO(ニトリロトリスメチレンホスホン酸)、HEDPO(ヒドロキシエチリデンジ(メチレンホスホン酸))、これらのアンモニウム塩、これらとアミンとの錯塩等のポリホスホン酸類、例えばEDDPO(エチレンジアミンジ(メチレンホスホン酸))、EDTPO(エチレンジアミンテトラ(メチレンホスホン酸))、PDTPPO(ジアミノプロパンテトラ(メチレンホスホン酸))、DETTPPO(ジエチレントリアミンペンタ(メチレンホスホン酸))、TTHPO(トリエチレンテトラミンヘキサ(メチレンホスホン酸))、これらのアンモニウム塩、これらとアミンとの錯塩等のアミノポリホスホン酸類等のホスホン酸類等が挙げられる。なかでも、EDTA、CyDTA、HEDPO、EDTPO、DETTPPO、これらのアンモニウム塩、及びこれらとアミンとの錯塩が特に好ましい。尚、上記に於いて、錯塩を形成するアミンとしては、先に述べたアミンと同じものが挙げられる。また、これらキレート剤は、単独で使用しても、2種以上適宜組み合わせ用いてもよい。キレート剤の使用量は、キレート剤の種類によって異なるため一概には言えないが、例えば通常0.0001~10重量%、好ましくは0.0001~1重量%、より好ましくは0.0001~0.5重量%である。

【0055】本発明に於いて用いられる界面活性剤とし

ては、通常この分野で用いられるものであればよく、特に限定されない。界面活性剤を添加することにより、基板表面に対する水性溶液の濡れ性を改善し得る。このような界面活性剤としては、例えば分子中にポリオキシアルキレン基を有するノニオン系界面活性剤、例えば分子中にスルホン酸基、カルボキシル基、ホスホン酸基、スルホキシル基及びホスホノキシル基から選ばれる基を有するアニオン系界面活性剤、例えばアルキルアミン、例えばアルキルトリメチルアンモニウム、アルキルジメチルベンジルアンモニウム等の第四級アンモニウム、例えばアルキルピリジニウム、これらの塩（例えば塩酸塩、硫酸塩等）等のカチオン系界面活性剤、例えばアルキルベタイン誘導体、イミダゾリニウムベタイン誘導体、スルホベタイン誘導体、アミノカルボン酸誘導体、イミダゾリン誘導体、アミノオキサイド誘導体等の両性界面活性剤等が挙げられるが、これらに限定されない。分子中にポリオキシアルキレン基を有するノニオン系界面活性剤としては、例えばポリオキシアルキレンアルキルエーテル、ポリオキシアルキレンポリアルキルアリアルエーテル等が挙げられ、より具体的には、例えばポリオキシエチレンアルキルエーテル、ポリオキシエチレンアルキルフェニルエーテル等の分子中にポリオキシエチレン基を有するノニオン系界面活性剤、例えばポリオキシプロピレンアルキルエーテル、ポリオキシプロピレンアルキルフェニルエーテル等の分子中にポリオキシプロピレン基を有するノニオン系界面活性剤、例えばポリオキシエチレンポリオキシプロピレンアルキルエーテル、ポリオキシエチレンポリオキシプロピレンアルキルフェニルエーテル等の分子中にポリオキシエチレン基及びポリオキシプロピレン基を有するノニオン系界面活性剤等が挙げられる。分子中にスルホン酸基、カルボキシル基、ホスホン酸基、スルホキシル基及びホスホノキシル基から選ばれる基を有するアニオン系界面活性剤としては、例えばアルキルスルホン酸、アルキルベンゼンスルホン酸、アルキルナフタレンスルホン酸、これらの塩（例えばナトリウム、カリウム等のアルカリ金属塩、例えばアンモニウム塩等、なかでもアンモニウム塩が好ましい）等の分子中にスルホン酸基を有するアニオン系界面活性剤、例えばアルキルカルボン酸、アルキルベンゼンカルボン酸、アルキルナフタレンカルボン酸、これらの塩（例えばナトリウム、カリウム等のアルカリ金属塩、例えばアンモニウム塩等、なかでもアンモニウム塩が好ましい）等の分子中にカルボキシル基を有するアニオン系界面活性剤、例えばアルキルホスホン酸、アルキルベンゼンホスホン酸、アルキルナフタレンホスホン酸、これらの塩（例えばナトリウム、カリウム等のアルカリ金属塩、例えばアンモニウム塩等、なかでもアンモニウム塩が好ましい）等の分子中にホスホン酸基を有するアニオン系界面活性剤、例えばアルキル硫酸エステル、アルキルベンゼン硫酸エステル、ポリオキシエチレンアルキル硫酸エ

ステル、ポリオキシエチレンアルキルベンゼン硫酸エステル、ポリオキシエチレンアルキルナフタレン硫酸エステル、これらの塩（例えばナトリウム、カリウム等のアルカリ金属塩、例えばアンモニウム塩等、なかでもアンモニウム塩が好ましい）等の分子中にスルホキシル基を有するアニオン系界面活性剤等が挙げられる。なかでも、ノニオン系界面活性剤及びアニオン系界面活性剤が好ましい。またノニオン系界面活性剤としてはポリオキシアルキレンアルキルエーテルが特に好ましく、アニオン系界面活性剤としては、分子中にスルホン酸基を有するもの、分子中にスルホキシル基を有するものが特に好ましい。より具体的にはポリオキシエチレンアルキルエーテル等の分子中にポリオキシエチレン基を有するノニオン系界面活性剤、ポリオキシエチレンポリオキシプロピレンアルキルエーテル等の分子中にポリオキシエチレン基及びポリオキシプロピレン基を有するノニオン系界面活性剤、アルキルベンゼンスルホン酸等の分子中にカルボキシル基を有するアニオン系界面活性剤、ポリオキシエチレンアルキル硫酸エステル等の分子中にスルホキシル基を有するアニオン系界面活性剤が特に好ましい。また、これら界面活性剤は、単独で使用しても、2種以上適宜組み合わせ用いてもよい。界面活性剤の使用量は、界面活性剤の種類によって異なるため一概には言えないが、ノニオン系界面活性剤は、臨界ミセル濃度以上であればよく、それより薄ければエッチングの速度が速くなり、効果が薄れる。また、ノニオン系界面活性剤以外の界面活性剤は、基板表面処理剤の表面張力を低下させ得る量であればよい。具体的な使用量としては、界面活性剤の種類により異なるため一概には言えないが、通常0.0001~1重量%、好ましくは0.0001~0.1重量%、より好ましくは0.0001~0.05重量%である。

【0056】本発明の金属腐蝕防止剤は、上記した如き本発明に係るアミノ酸又はその誘導体と、上記した如き有機酸、アミン、無機アルカリ化合物、キレート剤及び界面活性剤のうちの少なくとも一つとを含んでなるものが好ましく、更には、上記した如き本発明に係るアミノ酸又はその誘導体と、キレート剤又は/及び界面活性剤とを含んでなるものが特に好ましい。

【0057】本発明の金属腐蝕防止剤は、そこに含まれる本発明に係る分子内にチオール基を有するアミノ酸又はその誘導体が有する、金属表面に吸着して当該表面に保護膜を形成することによって、金属表面を保護して水溶液や空気中から受ける金属の酸化や腐蝕を抑制し得るという性質を利用したものであり、本発明の金属腐蝕防止剤を用いて、例えば表面に金属被覆部を有する基板表面を処理すれば、当該基板表面の金属の酸化や腐食を防止し得、更には基板表面の金属不純物を有効に除去し得る。

【0058】本発明の処理剤は、上記した如き本発明の金属腐蝕防止剤、即ち、本発明に係る分子内にチオール



基を有するアミノ酸又はその誘導体、要すれば、例えば前述した如き、有機酸、アミン、無機アルカリ化合物、キレート剤、界面活性剤等の通常この分野で用いられる試薬類を前述した如き濃度範囲で含んでなるものである。尚、上記した如き通常この分野で用いられる試薬類のうちの少なくとも一つを、本発明の処理剤中に含有させれば、基板表面の金属の酸化や腐蝕を防止すると同時に、金属不純物（例えば酸化銅、酸化鉄等の金属酸化物等）やパーティクル等をより有効に除去し得る。なかでも、上記した如き本発明に係るアミノ酸又はその誘導体と、キレート剤又は／及び界面活性剤とを含んでなるものが特に好ましい。上記した如き試薬類の具体例、好ましい態様等は先に述べた通りである。

【0059】本発明の処理剤は、通常水性溶液の状態であり、前述した如き本発明の金属腐蝕防止剤と同様の調製方法により、当該本発明に係るアミノ酸又はその誘導体を水に添加溶解させることにより調製される。

【0060】このように調製された本発明の処理剤は、使用前に濾過処理等を行うのが好ましい。

【0061】本発明の処理方法（金属腐蝕防止方法）は、上記した如き本発明の処理剤（金属腐蝕防止剤）と、表面に金属被覆部を有する基板表面の金属とを接触させて、当該基板表面を本発明の処理剤（金属腐蝕防止方法）で処理すればよい。

【0062】表面に金属被覆部を有する基板表面を、本発明の処理剤（金属腐蝕防止方法）で処理する方法としては、通常この分野で行われる自体公知の方法であればよく、具体的には、単に基板を処理剤（金属腐蝕防止剤）中に浸漬するディップ処理、基板に処理剤をシャワー状に振りかける枚葉処理等の方法が挙げられる。

【0063】本発明に於いて、「処理」とは、上記したように、本発明の処理剤と基板表面の金属とを接触させることをいう。より具体的には、例えば保存処理、例えば洗浄処理等に付す前の前処理、洗浄処理等が挙げられるが、これらに限定されるものではない。

【0064】即ち、本発明の金属腐蝕防止剤は、例えば表面に金属被覆部を有する基板用の保存剤、又は表面に金属被覆部を有する基板用の前処理剤、或いは表面に金属被覆部を有する基板用の洗浄剤等の処理剤としても使用し得る。

【0065】例えば本発明の処理剤を、表面に金属被覆部を有する基板用の保存剤として用いれば、水溶液や空気等の各種雰囲気から、基板保存中に当該金属が受ける酸化や腐蝕を防止することができ、更には基板表面の金属不純物をも有効に除去することができる。本発明の基板の保存方法としては、例えば上記した如きディップ処理等を行って本発明の処理剤（保存剤）中に基板を浸漬したまま保存する方法、上記した如き枚葉処理等を行って本発明の処理剤（保存剤）を基板に振りかけたまま保存する方法、或いはこれらの処理を行った後、基板を乾

燥して保存する方法等が挙げられる。

【0066】また、例えば本発明の処理剤を、例えば表面に金属被覆部を有する基板を洗浄工程等に共する前に、当該基板用の前処理剤として用いて基板表面の金属を処理すれば、次工程で用いられる洗浄剤等の水溶液や次工程に共される間の空気等の各種雰囲気から、次工程の過程に金属が受ける酸化や腐蝕を防止することができ、更には、超純水による洗浄等の簡単な操作によって、基板表面の金属不純物を有効に除去することができる。本発明の基板の前処理方法としては、例えば上記した如きディップ処理により本発明の処理剤（前処理剤）中に基板を浸漬する方法、上記した如き枚葉処理により本発明の処理剤（前処理剤）を基板に振りかける方法、或いはこれらの処理を行った後、基板を乾燥する方法等が挙げられる。

【0067】このようにして得られた基板は、通常この分野で行われる自体公知の表面処理剤（洗浄剤）を用いる洗浄方法に共することができる。上記に於いて用いられる表面処理剤（洗浄剤）としては、この分野で用いられるものは全て使用することができ、特に限定されないが、例えば特開平5-263275号公報、特開平6-112646号公報、特開平6-287774号公報、特開平7-54169号公報、特開平7-79061号公報、特開平7-166381号公報、特開平7-92483号公報、特開2000-8185号公報、特開平10-251867号公報、特開平7-267933号公報、特開平11-50275号公報等に記載された表面処理剤（洗浄剤）、後述する本発明の洗浄剤等が挙げられる。

【0068】更に、例えば本発明の処理剤を、例えば表面に金属被覆部を有する基板用の洗浄剤として用いて、表面に金属被覆部を有する基板表面を処理すれば、基板表面の金属の腐蝕や酸化を防止し得、且つ当該表面の金属不純物を有効に除去し得る。

【0069】本発明の処理剤は、前述したように、本発明に係る分子内にチオール基を有するアミノ酸又はその誘導体と、前述した如き、有機酸、アミン、無機アルカリ化合物、キレート剤及び界面活性剤のうちの少なくとも一つとを含んでなるものが好ましく、本発明に係るアミノ酸又はその誘導体と、キレート剤又は／及び界面活性剤とを含んでなるものがより好ましいが、本発明の処理剤を、洗浄剤として使用する際には、このような組成とするのが特に好ましい。尚、上記した如き有機酸、アミン、無機アルカリ化合物、キレート剤及び界面活性剤の具体例、好ましい態様等は先に述べた通りである。

【0070】本発明の洗浄剤は、通常水性溶液の状態であり、当該本発明に係るアミノ酸又はその誘導体（又はこれと、有機酸、アミン、無機アルカリ化合物、キレート剤及び界面活性剤のうちの少なくとも一つと）を、水に添加溶解させることにより調製される。本発明に係るアミノ酸又はその誘導体を水に溶解する方法としては、例えば水の中に、別途溶解した本発明に係るアミノ酸又

はその誘導体（又はこれと、別途溶解した有機酸、アミン、無機アルカリ化合物、キレート剤及び界面活性剤のうちの少なくとも一つと）を添加する方法や、本発明に係るアミノ酸又はその誘導体（又はこれと、有機酸、アミン、無機アルカリ化合物、キレート剤及び界面活性剤のうちの少なくとも一つと）を直接水に添加し、溶解、攪拌する方法、或いは、水の中に添加、溶解した本発明に係るアミノ酸又はその誘導体と、別途水の中に添加、溶解した、有機酸、アミン、無機アルカリ化合物、キレート剤及び界面活性剤のうちの少なくとも一つとを、攪拌、混合する方法等が挙げられる。

【0071】このようにして調製した本発明の洗浄剤は、使用前に濾過処理等を行うのが好ましい。また、ここで用いられる水は、蒸留、イオン交換処理等により精製されたものであればよいが、この分野で用いられる、いわゆる超純水がより好ましい。

【0072】本発明の洗浄方法は、表面に金属被覆部を有する基板表面を、上記した如き本発明の洗浄剤で処理すればよい。

【0073】表面に金属被覆部を有する基板表面を、本発明の洗浄剤で処理する方法としては、通常この分野で行われる自体公知の洗浄方法であればよく、例えば前述した如きディップ処理、枚葉処理等の方法が挙げられる。

【0074】更に、本発明に於いては、洗浄時に物理的洗浄を併用することにより、より効果的に金属不純物（酸化同等の金属酸化物等）を除去することができる。併用の具体的方法としては、表面に金属被覆部を有する基板表面を、本発明の洗浄剤の存在下、物理的洗浄工程に付すこと等が挙げられる。

【0075】上記方法に於いて、本発明の洗浄剤を存在させる方法としては、具体的には、上記した如きディップ処理、枚葉処理等により本発明の洗浄剤を存在させた状態として物理的洗浄工程に付す方法等が挙げられる。また、物理的洗浄（工程）としては、例えば高速回転のポリビニルアルコール製ブラシ等を用いて基板表面を洗浄するブラシスクラブ洗浄、高周波を用いるメガソニック洗浄等が挙げられる。

【0076】物理的洗浄を併用する場合のより具体的な手法としては、例えば基板を本発明の洗浄剤中に浸漬した後、当該洗浄液中から取り出して基板表面に当該洗浄剤を存在させた状態とした後に物理的洗浄を行う方法、基板を本発明の洗浄剤中に浸漬させたまま物理的洗浄を行う方法、基板表面に本発明の洗浄剤を振りかけて基板表面に当該洗浄剤を存在させた状態とした後に物理的洗浄を行う方法、或いは基板表面に本発明の洗浄剤を振りかけながら物理的洗浄を行う方法等が挙げられる。

【0077】上記した如き本発明の金属腐蝕防止剤及び処理剤（保存剤、前処理剤、洗浄剤等）の液性は特に限定されず、用いられる基板の種類や使用目的等により通

常この分野で用いられるpH範囲から適宜選択される。より具体的には、弱酸性乃至アルカリ性が好ましく、通常pH2~13、好ましくはpH3~12、より好ましくはpH4~10である。このようなpH範囲とすることで、基板表面とパーティクルとの電気的な反発が大きくなるので、パーティクル及び金属不純物（例えば酸化銅等の金属酸化物等）の除去効果が向上し、更には層間絶縁膜であるSiO<sub>2</sub>をエッチングする恐れがより少なくなる。

【0078】本発明の金属腐蝕防止剤及び処理剤（保存剤、前処理剤、洗浄剤等）は、例えば表面に金属被覆部を有する基板に使用し得る。このような基板としては、例えば半導体基板、ポリイミド樹脂等のプリント基板、LCD等を使用されるガラス基板等が挙げられ、特に半導体基板に有用である。また、当該基板表面に被覆される金属としては、硫黄と反応する金属であればよく、例えば銅、クロム、銀、金等が挙げられ、特に金属銅に有用である。なかでも、表面に銅被覆部を有する（銅配線が施された）半導体基板に特に有用である。

【0079】以下に実施例及び比較例を挙げるが、本発明はこれらにより何等限定されるものではない。

【0080】また、本実施例及び比較例に於いて使用した金属Cu堆積ウェーハ及びCu汚染ウェーハは夫々以下の方法により調製したものを使用し、また、金属Cu堆積ウェーハ表面のCuの膜厚及びCu汚染ウェーハ表面に吸着残存しているCu（銅原子）の吸着量（残存Cu濃度）は夫々以下の方法により測定した。

【0081】〔金属Cu堆積ウェーハ〕4インチシリコンウェーハの表面にスパッタ法により金属Cuを堆積させたものを銅堆積ウェーハとした。尚、下記に示す方法により当該金属Cu堆積ウェーハ表面の銅の膜厚は、1000nmであることを確認した。

【0082】〔Cu汚染ウェーハ〕熱酸化法により表面をSiO<sub>2</sub>とした4インチシリコンウェーハを、1ppmとなるようにCuイオンを添加したスラリー水溶液（1%シリカ含有0.1%過酸化水素水）1Lに1分間浸漬し、超純水により10分間流水洗浄した後、スピン乾燥したものをCu汚染ウェーハとした。尚、下記に示す方法により、当該Cu汚染ウェーハには、Cu（銅原子）が $3 \times 10^{14}$ 原子/cm<sup>2</sup>吸着残存していることを確認した。

【0083】〔金属Cu膜厚測定法〕ウェーハを半分に割り、断面を電子顕微鏡により観察し、金属Cu膜厚を測定した。

【0084】〔Cu濃度測定法〕ウェーハ表面に吸着残存したCuを、フッ酸-硝酸水溶液で溶解回収した後、該回収液中のCu濃度を、原子吸光法（黒鉛炉原子吸光分光分析装置）により測定した。得られた測定値に基づいてCu（銅原子）の吸着量（残存Cu濃度）を求めた。

【0085】尚、本実施例及び比較例に於いては、特に断りのない限り濃度を表す%、ppm、ppbは全て重量比を示す。また、使用する水は全て超純水であり、銅が0.01

ppb以下であることを確認してから使用した。

【0086】

【実施例】実施例1～14

表1に記載の各金属腐蝕防止剤（保存剤）1Lに、上記方法で作製した金属Cu堆積ウェーハを室温下、5時間浸漬した。その後、ウェーハを取り出し、超純水で10分間リンスし、スピン乾燥させた。このように処理した金

属Cu堆積ウェーハについて、金属Cuの酸化の有無を確認するため、ウェーハ表面のCu膜表面の色調を目視で観察し、また、金属Cuの腐蝕の有無を確認するため、ウェーハ表面の金属Cuの膜厚を測定した。結果を表1に示す。

【0087】

【表1】

	金属腐蝕防止剤 (濃度：重量%)	Cu膜表面の 色調	Cu膜厚 (nm)
実施例1	システイン(0.05)	変化なし	940
実施例2	システインメチルエステル (0.001)	変化なし	950
実施例3	システインエチルエステル (0.001)	変化なし	980
実施例4	ホモシステイン(0.001)	変化なし	1000
実施例5	システイン(0.01) シュウ酸(0.3)	変化なし	1000
実施例6	システイン(0.001) エチレンジアミン(0.001)	変化なし	980
実施例7	アセチルシステイン(0.05) アンモニア(0.1)	変化なし	950
実施例8	アセチルシステイン(0.01) EDTA(0.001)	変化なし	1000
実施例9	システイン(0.1) TTHPO(0.01)	変化なし	970
実施例10	システイン(0.001) ポリオキシエチレンアルキルエー テル(アルキル C=8~12)(0.0001)	変化なし	950
実施例11	システイン(0.01) アルキルナフタレンカルボン酸 (0.0001)	変化なし	1000
実施例12	システイン(0.01) ヒドロキシルアミン(0.005) EDTPO(0.05)	変化なし	940
実施例13	システイン(0.01) シュウ酸(0.5) CyDTA(0.001) ポリオキシエチレンアルキル硫酸 エステル(0.01)	変化なし	960
実施例14	アセチルシステイン(0.001) クエン酸(1.0) HEDPO(0.05) キルスルホン酸(0.0001)	変化なし	980

【0088】比較例1～6

表2に記載の各種溶液を用いた以外は、実施例1～14

と同様の方法で金属Cu堆積ウェーハを処理した後、ウェー

ハ表面のCu膜表面の色調を目視で観察し、また、ウェー

ハ表面の金属Cuの膜厚を測定した。結果を表2に示す。尚、表2中の－は測定不能を示す。

【0089】

【表2】

	溶液 (濃度：重量%)	Cu膜表面の 色調	Cu膜厚 (nm)
比較例1	水	光沢消失	—
比較例2	シュウ酸(0.01)	光沢消失	330
比較例3	アンモニア(0.01)	Cu膜溶解	0
比較例4	NiPO(1.0)	変化なし	550
比較例5	ポリオキシエチレンアルキルベン ゼン硫酸エステル(0.1)	光沢消失	—
比較例6	クエン酸(1.0) IDA(0.05) ポリオキシプロピレンアルキル エーテル(0.01)	変化なし	770

【0090】表1及び表2から明らかなように、本発明の金属腐蝕防止剤（保存剤）（実施例1～14）中で金属Cu堆積ウェーハを保存した場合には、ウェーハ表面のCu膜表面の色調に変化はなく、金属Cuが酸化されておらず、且つCu膜厚に殆ど変化が無く、金属Cuが腐蝕されていないことが判る。これに対して、比較例1及び5の溶液中で金属Cu堆積ウェーハを保存した場合には、金属Cuが著しく腐蝕され、且つウェーハ表面のCu膜表面の光沢が消失し、金属Cuが酸化されていることが判る。また、比較例4及び6の溶液中で保存した場合には、ウェーハ表面のCu膜表面の色調に変化はなく、金属Cuが酸化されてはいないものの、Cu膜厚が減少し、金属Cuが腐蝕（溶解）されていることが判る。更には、比較例2に於いては、金属Cuが酸化及び腐蝕（溶解）されていることが、特に比較例3に於いては、金属Cuが全て腐蝕（溶解）されていることが判る。即ち、本発明の金属腐蝕防止剤は、金属の酸化と腐食を防止し得、本発明の金属防止剤を含んでなる処理剤（保存剤）中で表面に金属被覆部を有する基板を保存すれば、当該金属の酸化と腐食を同時に防止し得、表面に金属被覆部を有する基板を溶液中で良好に保存し得ることが判る。

#### 【0091】実施例15～17

表3に記載の各金属腐蝕防止剤（保存剤）1Lに、上記方法で作製した金属Cu堆積ウェーハを室温下、1分間浸漬した。その後、ウェーハを取り出し、超純水で10分間リンスし、スピン乾燥させた。次いで、ウェーハを空气中で10時間放置した。このように処理した金属Cu堆積ウェーハについて、金属Cuの酸化の有無を確認するため、ウェーハ表面のCu膜表面の色調を目視で観察した。結果を表3に示す。

#### 【0092】比較例7～10

表3に記載の各種溶液を用いた以外は、実施例15～17と同様の方法で金属Cu堆積ウェーハを処理した後、ウェーハ表面のCu膜表面の色調を目視で観察した。結果を表3に実施例15～17と併せて示す。

#### 【0093】

【表3】

	金属腐蝕防止剤又は溶液 (濃度：重量%)	Cu膜表面の 色調
実施例15	システイン(0.05)	変化なし
実施例16	システイン(0.01) マロン酸(0.3) DETPPO(0.005)	変化なし
実施例17	システイン(0.001) エチレンジアミン(0.1) PDTPO(0.05) ポリオキシエチレンポリオキシ プロピレンアルキルエーテル (0.002)	変化なし
比較例7	水	光沢消失
比較例8	シュウ酸(0.3)	光沢消失
比較例9	アンモニア(0.01)	光沢消失
比較例10	マロン酸(0.5) EDDPO(0.01) アルキルナフタレンカルボン酸 (0.001)	光沢消失

【0094】表3から明らかなように、本発明の金属腐蝕防止剤（保存剤）（実施例15～17）で金属Cu堆積ウェーハを処理した後に、当該ウェーハを空气中で保存した場合には、ウェーハ表面のCu膜表面の色調に変化はなく、金属Cuが酸化されていないことが判る。これに対して、比較例7～10の溶液で金属Cu堆積ウェーハを処理した場合には、ウェーハ表面のCu膜表面の光沢が消失し、金属Cuが酸化されていることが判る。即ち、本発明の金属防止剤を含んでなる処理剤（保存剤）で、表面に金属被覆部を有する基板を処理した後、これを保存すれば、当該基板表面の金属の酸化を防止し得、表面に金属被覆部を有する基板を空气中で良好に保存し得ることが判る。

#### 【0095】実施例18～20

表4に記載の各金属腐蝕防止剤（保存剤）500mlを、上記方法で作製した金属Cu堆積ウェーハ表面に1分間かけて振りかけた。その後、ウェーハを、超純水で10分間リンスし、スピン乾燥させた。次いで、ウェーハを空气中で10時間放置した。このように処理した金属Cu堆積ウェーハについて、金属Cuの酸化の有無を確認するため、ウェーハ表面のCu膜表面の色調を目視で観察した。結果を表4に示す。

#### 50 【0096】比較例11～14

表 4 に記載の各種溶液を用いた以外は、実施例 18 ～ 20 と同様の方法で金属 Cu 堆積ウェーハを処理した後、ウェーハ表面の Cu 膜表面の色調を目視で観察した。結果を表 4 に実施例 18 ～ 20 と併せて示す。

【 0 0 9 7 】

【表 4】

	金属腐蝕防止剤又は溶液 (濃度 : 重量%)	Cu 膜表面の 色調
実施例 18	システイン(0.05)	変化なし
実施例 19	アセチルシステイン(0.01) 酒石酸(0.1) EDTA-OH(0.01) ポリオキシエチレンアルキルベン ゼン硫酸エステル(0.05)	変化なし
実施例 20	システイン(0.1) シクロヘキシルアミン(0.1) TTHA(0.005)	変化なし
比較例 11	水	光沢消失
比較例 12	シュウ酸(0.3)	光沢消失
比較例 13	アンモニア(0.01)	光沢消失
比較例 14	リンゴ酸(0.2) DETPPO(0.01) アルキルベンゼンスルホン酸 (0.001)	光沢消失

【 0 0 9 8 】 表 4 から明らかなように、本発明の金属腐蝕防止剤（保存剤）（実施例 18 ～ 20）で金属 Cu 堆積ウェーハを処理した後に、当該ウェーハを空气中で保存した場合には、ウェーハ表面の Cu 膜表面の色調に変化はなく、金属 Cu が酸化されていないことが判る。これに対して、比較例 15 ～ 17 の溶液で金属 Cu 堆積ウェーハを処理した場合には、ウェーハ表面の Cu 膜表面の光沢が消失し、金属 Cu が酸化されていることが判る。即ち、実施例 15 ～ 17 で行った如きいわゆるディップ処理だけでなく、実施例 18 ～ 20 で行ったようないわゆる枚葉処理によっても、本発明の金属防止剤を含んでなる処理剤（保存剤）で、表面に金属被覆部を有する基板を処理し

た後、これを保存すれば、当該基板表面の金属の酸化を防止し得、表面に金属被覆部を有する基板を空气中で良好に保存し得ることが判る。

【 0 0 9 9 】 実施例 21 ～ 34

表 5 に記載の各金属腐蝕防止剤（前処理剤）1 L に、上記方法で作製した Cu 汚染ウェーハ及び金属 Cu 堆積ウェーハを室温下、1 時間浸漬した。その後、ウェーハを取り出し、超純水で 10 分間リンスし、スピン乾燥させた。次いで、表 5 に記載の各洗浄液 1 L に、当該ウェーハを室温下、10 分間浸漬した。その後、ウェーハを取り出し、超純水で 10 分間リンスし、スピン乾燥させた。このように処理した Cu 汚染ウェーハについては、金属不純物除去能力を評価するため、ウェーハ表面に吸着残存している残存 Cu 濃度を測定し、また、金属 Cu 堆積ウェーハについては、金属 Cu の酸化の有無を確認するため、ウェーハ表面の Cu 膜表面の色調を目視で観察し、更に、金属 Cu の腐蝕の有無を確認するため、ウェーハ表面の金属 Cu の膜厚を測定した。結果を表 5 に示す。尚、表 5 中の一は測定不能を示す。

20 【 0 1 0 0 】 比較例 15 ～ 25

表 6 に記載の各種溶液及び各洗浄剤を用いた以外は、実施例 21 ～ 34 と同様の方法で Cu 汚染ウェーハ及び金属 Cu 堆積ウェーハを処理した後、Cu 汚染ウェーハについては、ウェーハ表面に吸着残存している残存 Cu 濃度を測定し、また、金属 Cu 堆積ウェーハについては、ウェーハ表面の Cu 膜表面の色調を目視で観察し、更に、ウェーハ表面の金属 Cu の膜厚を測定した。結果を表 6 に示す。尚、比較例 15 ～ 18 に於いては、金属腐蝕防止剤（前処理剤）での処理を行わず、表 6 に記載の各洗浄液 1 L に、当該ウェーハを室温下、10 分間浸漬した後、ウェーハを取り出し、超純水で 10 分間リンスし、スピン乾燥させたものを測定・観察した。

【 0 1 0 1 】

【表 5】

	金属腐蝕防止剤 (濃度 : 重量%)	洗浄剤 (濃度 : 重量%)	残存Cu濃度 (Cu原子/cm <sup>2</sup> )	Cu膜表面の 色調	Cu膜厚 (nm)
実施例21	システイン(0.01)	クエン酸(10.0) HEDPO(0.5)	$2 \times 10^{10}$	変化なし	1000
実施例22	アセチルシステイン(0.01) クエン酸(1.0)	アルキルナフタレンスルホン酸アンモニウム(0.01)	$1 \times 10^{10}$	変化なし	1000
実施例23	アセチルシステイン(0.1) アンモニア(1.0)	トリエチレンテトラミン (0.05) シクロヘキシルアミンジ (ポリオキシエチレン) (0.001)	$8 \times 10^9$	変化なし	970
実施例24	システイン(0.01) シュウ酸(0.3)	クエン酸(3.0)	$8 \times 10^{10}$	変化なし	1000
実施例25		リンゴ酸(0.5) DETPPO(0.002)	$6 \times 10^{10}$	変化なし	1000
実施例26		シュウ酸(0.5) アルキルスルホン酸(0.001)	$8 \times 10^{10}$	変化なし	920
実施例27		クエン酸(10.0) HEDPO(0.5) アルキルナフタレンスルホン酸アンモニウム(0.01)	$5 \times 10^9$ 以下	変化なし	1000
実施例28		ジエチレントリアミン(1.0)	$9 \times 10^9$	変化なし	920
実施例29		TMAH(0.005) GEDTA(0.05)	$8 \times 10^{10}$	変化なし	1000
実施例30		トリエチレンテトラミン (0.05) シクロヘキシルアミンジ (ポリオキシエチレン) (0.001)	$5 \times 10^{10}$	変化なし	980
実施例31		水	$3 \times 10^{11}$	変化なし	1000
実施例32		NaOH(1.0)	$5 \times 10^{11}$	変化なし	1000
実施例33		EDTA(0.01)	$7 \times 10^{10}$	変化なし	1000
実施例34		ポリオキシエチレンノニル エーテル(0.01)	$5 \times 10^{11}$	変化なし	1000

	溶液 (濃度：重量%)	洗浄剤 (濃度：重量%)	残存Cu濃度 (Cu原子/cm <sup>2</sup> )	Cu膜表面の 色調	Cu膜厚 (nm)
比較例15	—	NaOH(1.0)	$7 \times 10^{13}$	変化なし	1000
比較例16		ポリオキシエチレンノニル エーテル(0.01)	$5 \times 10^{13}$	変化なし	1000
比較例17		シュウ酸(0.5) アルキルスルホン酸(0.001)	$5 \times 10^{13}$	変化なし	850
比較例18		ジエチレントリアミン(1.0)	$8 \times 10^{10}$	表面荒れ	450
比較例19	ベンゾトリアゾール(0.01)	クエン酸(10.0) HEDFO(0.5)	$2 \times 10^{10}$	表面荒れ	680
比較例20	ベンゾトリアゾール(0.5)	アルキルナフタレンスルホ ン酸アンモニウム(0.01)	$5 \times 10^{13}$	変化なし	1000
比較例21	イミダゾール(0.5)	トリエチレントトラミン (0.05)	$8 \times 10^9$	光沢消失	300
比較例22	3-アミノトリアゾール(0.05) アンモニア(1.0)	シクロヘキシルアミンジ (ポリオキシエチレン) (0.001)	$9 \times 10^9$	溶解	0
比較例23	キナリン酸(0.5) クエン酸(1.0)	クエン酸(10.0) HEDFO(0.5) アルキルナフタレンスルホ ン酸アンモニウム(0.01)	$4 \times 10^{11}$	光沢消失	800
比較例24	3-アミノ-5-メルカプトトリ アゾール(0.1) クエン酸(1.0)		$7 \times 10^{13}$	変化なし	1000
比較例25	2-メルカプトエタノール (0.01) クエン酸(1.0)		$8 \times 10^{13}$	変化なし	1000

【0103】表5及び表6の結果から明らかなように、実施例21、22及び27の金属腐蝕防止剤（前処理剤）を用いて前処理を行った場合は、Cu汚染ウェーハ表面の残存Cu濃度を $10^{10}$ オーダー以下に抑制し得、且つ金属Cuの酸化並びに腐蝕を防止し得ることが判る。これに対し、従来の金属腐蝕防止剤（表面処理剤）を用いて前処理を行った場合には、残存Cu濃度を同程度に抑制し得るものの、金属Cuの酸化や腐蝕を生じてしまったり（比較例19及び23）、金属Cuの酸化腐蝕は抑えられないものの、残存Cu濃度が高く、酸化銅を効果的に除去し得ない（比較例20、24及び25）ことが判る。同様に、実施例23及び30に於いては、酸化銅を効果的に除去し得、且つ金属Cuの酸化並びに腐蝕を防止し得るのに対し、比較例21及び22は、基板表面のCu膜が著しく腐蝕されているのが判る。また、実施例26、28、32及び34と比較例15～18との結果から、本発明の金属腐蝕防止剤（前処理剤）を用いて前処理を行えば、これを行わない場合に比べて洗浄時に於ける金属Cuの酸化及び腐蝕を抑制し得、更には酸化銅をも効果的に除去し得ることも判る。以上のことから明かなように、表面に金属被覆部を有する基板を洗浄工程に付す前に、本発明の金属腐蝕防止剤（前処理剤）を用いて当該基板を前処理すれば、洗浄工程に於いて金属が酸化や腐蝕を受けるのを防止することができ、更には、金属酸化物をも効果的に除去し得ることが判る。

【0104】実施例35～44

表7に記載の各洗浄剤（金属腐蝕防止剤）1Lに、上記方法で作製したCu汚染ウェーハを室温下、10分間浸漬した。その後、ウェーハを取り出し、超純水で10分間リンスし、スピン乾燥させた。また、表7に記載の各洗浄剤（金属腐蝕防止剤）1Lに、上記方法で作製した金属Cu堆積ウェーハを室温下、5時間浸漬した。その後、ウェーハを取り出し、超純水で10分間リンスし、スピン乾燥させた。このように処理したCu汚染ウェーハについては、金属不純物除去能力を評価するため、ウェーハ表面に吸着残存している残存Cu濃度を測定し、また、金属Cu堆積ウェーハについては、金属Cuの酸化の有無を確認するため、ウェーハ表面のCu膜表面の色調を目視で観察し、更に、金属Cuの腐蝕の有無を確認するため、ウェーハ表面の金属Cuの膜厚を測定した。結果を表7に示す。

【0105】比較例26～37

表8に記載の各洗浄剤を用いた以外は、実施例35～44と同様の方法でCu汚染ウェーハ及び金属Cu堆積ウェーハを処理した後、ウェーハ表面に吸着残存している残存Cu濃度を測定し、また、金属Cu堆積ウェーハについては、ウェーハ表面のCu膜表面の色調を目視で観察し、更に、ウェーハ表面の金属Cuの膜厚を測定した。結果を表8に示す。尚、表8中の—は測定不能を示す。

【0106】

【表7】

	洗浄剤 (濃度 : 重量%)	残存Cu濃度 (Cu原子/cm <sup>2</sup> )	Cu膜表面の 色調	Cu膜厚 (nm)
実施例35	システイン(0.1) シュウ酸(1.0)	$5 \times 10^{10}$	変化なし	980
実施例36	アセチルシステイン(0.001) 酒石酸(0.1) EDTA(0.001)	$2 \times 10^{10}$	変化なし	960
実施例37	システイン(0.001) リンゴ酸(0.5) NTA(0.005)	$8 \times 10^{10}$	変化なし	950
実施例38	アセチルシステイン(0.001) マロン酸(0.05) ETDPO(0.0001)	$9 \times 10^9$	変化なし	900
実施例39	システイン(0.001) クエン酸(3.0) HEDPO(0.5) ドデシルベンゼンスルホン酸(0.001)	$5 \times 10^9$ 以下	変化なし	1000
実施例40	システイン(0.01) シュウ酸(0.05) DETPPO(0.001) ポリオキシエチレンポリオキシプロピレンアルキルエーテル(0.001)	$5 \times 10^9$ 以下	変化なし	1000
実施例41	アセチルシステイン(0.01) リンゴ酸(0.05) ポリオキシエチレンドデシル硫酸エステル(0.0001)	$5 \times 10^9$ 以下	変化なし	1000
実施例42	L-システイン(0.01) ヒドロキシルアミン(0.01)	$1 \times 10^{10}$	変化なし	980
実施例43	D-システイン(0.02) シクロヘキシルアミンジ(ポリオキシエチレン) (2.0)	$3 \times 10^{10}$	変化なし	1000
実施例44	システイン(0.001) トリエチレントトラミン(0.2) ポリオキシエチレンノニルフェニルエーテル(0.01)	$4 \times 10^{10}$	変化なし	930



	洗浄剤 (濃度：重量%)	残存Cu濃度 (Cu原子/cm <sup>2</sup> )	Cu膜表面の 色調	Cu膜厚 (nm)
比較例26	水	$1 \times 10^{14}$	光沢消失	—
比較例27	シュウ酸(0.3)	$5 \times 10^{10}$	光沢消失	300
比較例28	リンゴ酸(0.05) ベンゾトリアゾール(0.01)	$7 \times 10^{11}$	表面荒れ	450
比較例29	シュウ酸(0.05) ベンゾトリアゾール(0.8)	$9 \times 10^{13}$	変化なし	850
比較例30	クエン酸(1.0) EDTA(0.001) ドデシルベンゼンスルホン酸(0.001)	$1 \times 10^{10}$	光沢消失	700
比較例31	ジエチレントリアミン(0.7)	$5 \times 10^{10}$	光沢消失	300
比較例32	ポリオキシエチレンアルキルエーテル (アルキル C=8~12)(0.01)	$8 \times 10^{13}$	光沢消失	—
比較例33	ヒドロキシルアミン(0.3) ポリオキシプロピレンアルキルエーテル (0.001)	$9 \times 10^{10}$	光沢消失	700
比較例34	アンモニア(1.0) NTA(0.01)	$9 \times 10^{10}$	溶解	0
比較例35	トリアゾール(0.01)	$8 \times 10^{13}$	変化なし	1000
比較例36	2-メルカプトイミダゾリン(0.001) クエン酸(1.0)	$9 \times 10^{13}$	変化なし	1000
比較例37	チオグリセロール(0.001) エチレンジアミン(0.1)	$5 \times 10^{13}$	変化なし	1000

【0108】表7及び表8から明らかなように、本発明の洗浄剤（金属腐蝕防止剤）（実施例35～44）を用いてウェーハを洗浄した場合には、ウェーハ表面の残存Cu濃度を $10^{10}$ オーダー以下に抑制し得、また、Cu膜表面の色調に変化はなく、金属Cuが酸化されておらず、且つCu膜厚に殆ど変化が無く、金属Cuが腐蝕されていないことが判る。これに対して、比較例27、30、31、33及び34の洗浄剤を用いた場合には、残存Cu濃度を $10^{10}$ オーダー以下に抑制し得るものの、金属Cuが酸化され、金属Cuが著しく腐蝕されていることが判る。また、比較例29、及び35～37の洗浄剤を用いた場合には、ウェーハ表面の金属Cuが酸化されておらず、また、金属Cuが殆ど腐蝕もされてはいないものの、残存Cu濃度が高く、ウェーハ表面の酸化銅を十分に除去し得ないことが判る。更には、比較例26及び32の洗浄剤を用いた場合には、金属Cuが腐蝕及び酸化され、また、残存Cu濃度が高く、ウェーハ表面の酸化銅を十分に

除去し得ないことが判る。比較例28の洗浄剤を用いた場合には、金属Cuが著しく腐蝕されており、また、ウェーハ表面の酸化銅を十分に除去し得ないことが判る。即ち、本発明の洗浄剤を用いて表面に金属被覆部を有する基板表面を洗浄すれば、当該金属の酸化と腐食を防止し得、且つ当該表面の金属不純物（酸化銅）を有効に除去し得ることが判る。

#### 【0109】

【発明の効果】以上の如く、本発明は良好な金属腐食防止作用を有し且つ安全性が高い金属腐蝕防止剤、及びこれを用いた、基板表面、特に、表面に銅配線が施された基板表面に於ける銅配線の酸化や腐蝕を防止し得る当該基板の処理方法、並びに、当該基板表面の銅配線の腐蝕や酸化を防止し得、且つ当該表面の金属不純物（酸化銅）を有効に除去し得る基板の洗浄方法を提供するものであり、本発明の金属腐蝕防止剤を用いれば、例えば半導体製造時における諸問題を解決できる。

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